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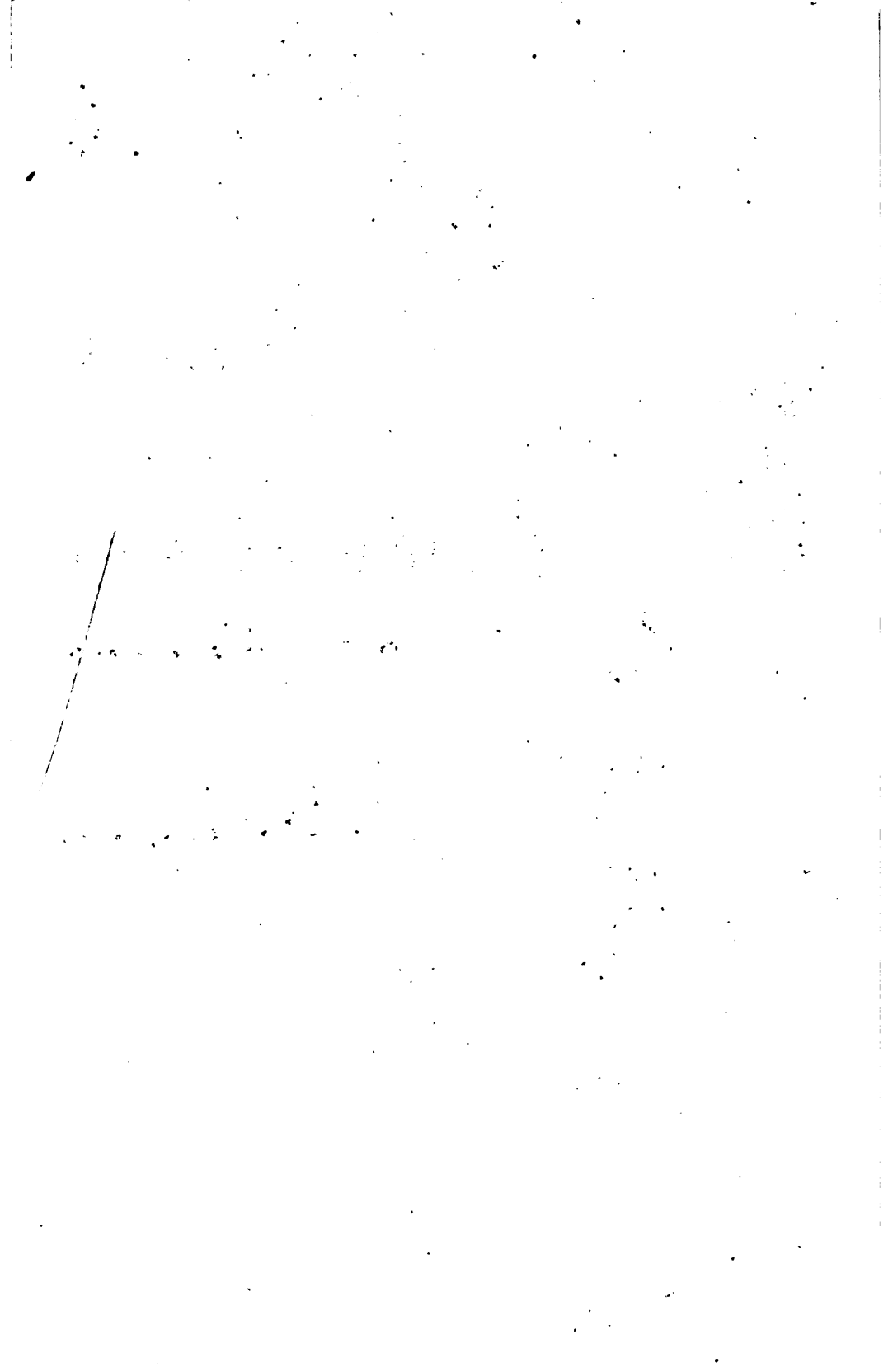
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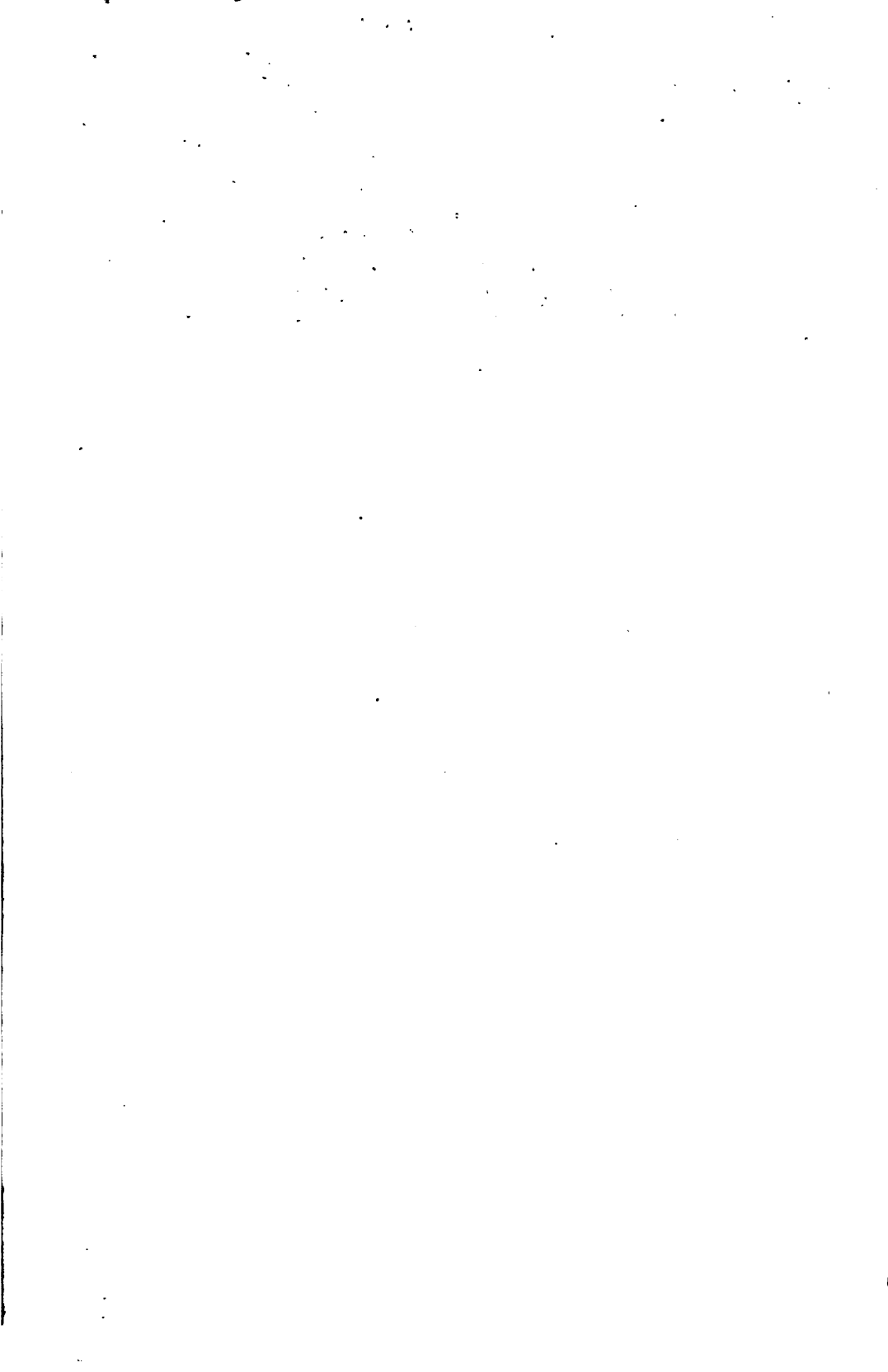


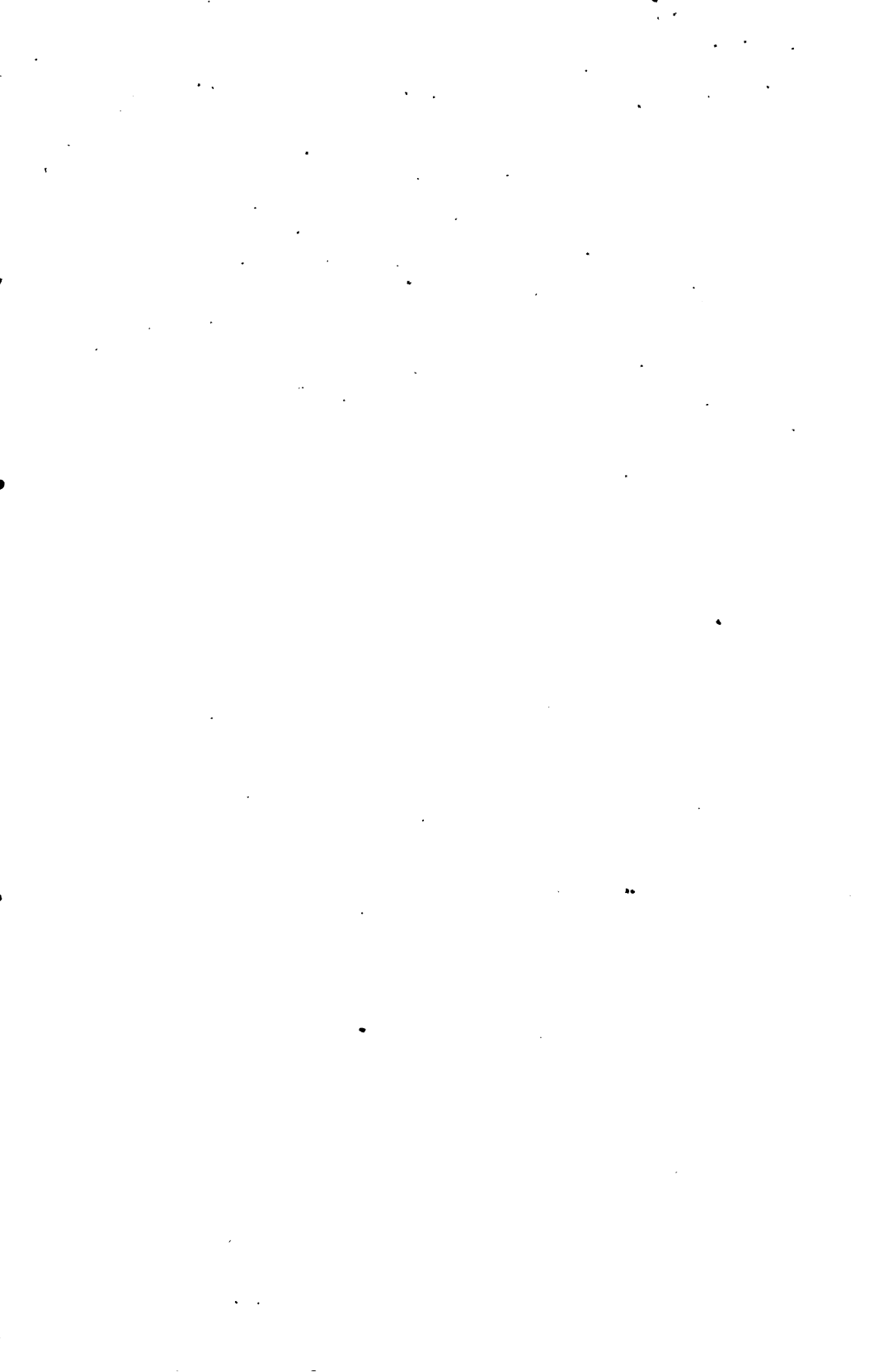
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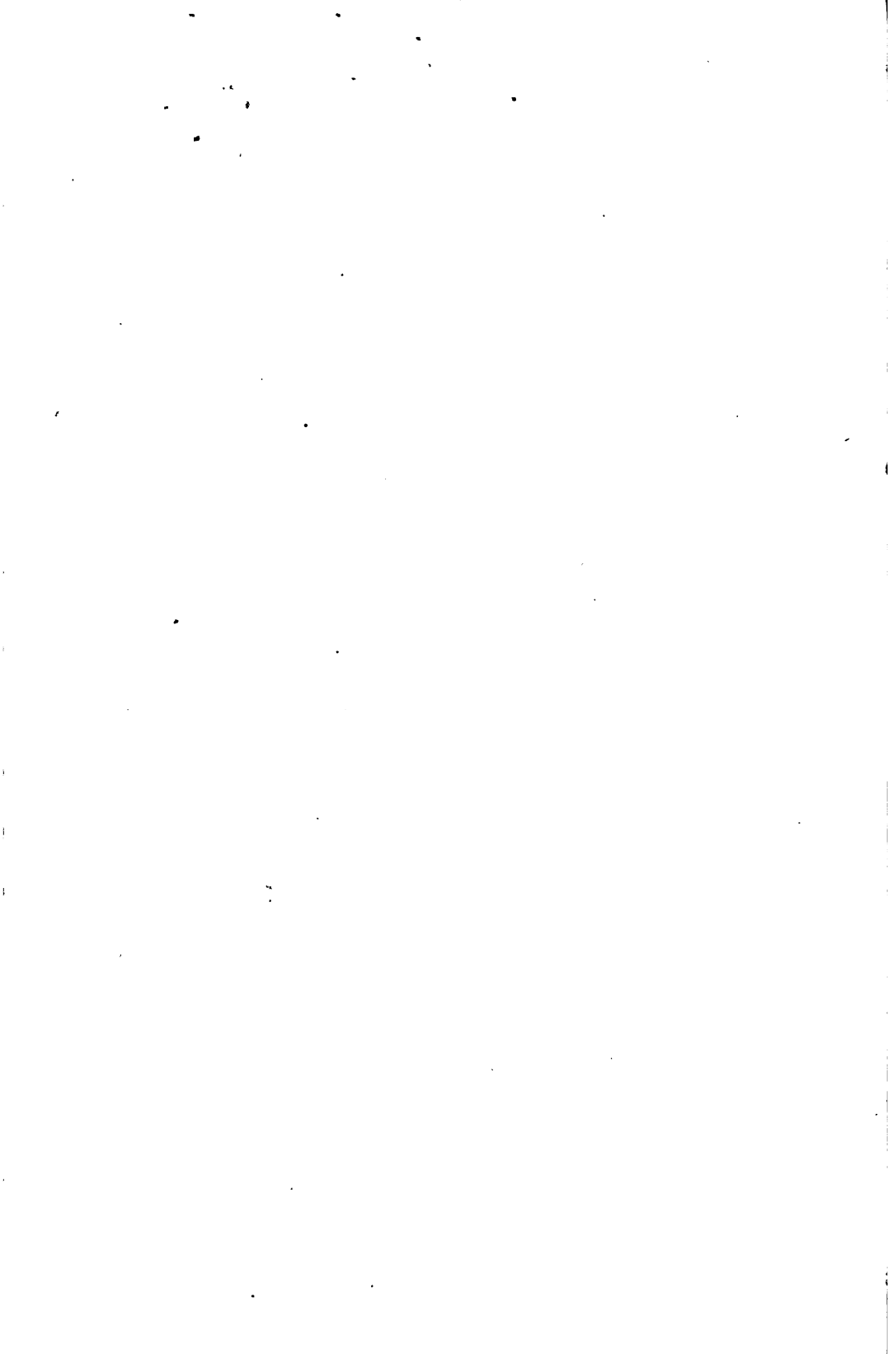
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THE
K I D N E Y S

AND

U R I N E.

BY

J. J. BERZELIUS.

TRANSLATED FROM THE GERMAN

BY

M. H. BOYÈ AND F. LEAMING M.D.

PHILADELPHIA:
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.....
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PREFACE

BY THE

TRANSLATORS.

Being engaged in the study of urine in various diseases, we have thought that a translation of the following article by Berzelius, extracted from his recently completed work on Animal Chemistry, would be acceptable to those of the medical profession who are engaged in similar investigations.

The study of the chemical nature of the urine in disease has only lately commenced. For a long time past physicians have examined it in diseases of the kidneys, but it is only within a few years that its importance has been understood in diseases of the system or of other organs than the kidneys. It has been well ascertained that the urine contains the effete matters resulting from the nutrition and waste of the different tissues; it will therefore indicate any derangement in either of these processes; and as it is a secretion easily obtained it claims much greater attention than it has hitherto received. In order to give a fuller view of the importance of the kidneys to the economy we will state that the urine is the only true excretion properly so called; for the perspiration may be supposed as intended rather to supply moisture to the surface, the respiration heat to the animal, and the fæces contain only the refuse or superfluous parts of the food.

The blood contains all the elements sufficient for the growth and preservation of the different organs. These organs differ not only in their functions but in their structure and composition, and hence will appropriate very different materials from the mass furnished in the blood. For instance the brain and nervous system will require its phosphorus and albumen, the muscular tissue its fibrin, the skin its gelatin, the membranes of the eye, the mucous and serous tissues its aqueous portions. It is obvious that the blood returning from the brain must be quite different from that returning from the muscles or skin. In the higher classes of animals the venous blood containing the effete matters of all the organs is passed through the lungs before it reaches the kidneys. This is not the case, however, with birds and amphibia, and it is worthy of remark, in passing, that their urine, secreted as it is from venous blood, contains large quantities of lithic acid with little or no urea, being the reverse of what exists in the healthy excretion of those animals whose kidneys are furnished with arterial blood. In man, then, the urine will contain the effete matters of the tissues, not as they have just come from them, but modified to a greater or less extent by respiration. The products of respiration are known to consist of carbonic acid and water; therefore the only alteration that can be produced in the effete matters is by their oxidation. Hence, even if the urine should not contain the original effete matters, its importance as a subject for pathological observation is not impaired: any material degree, for we still find the slightest derangements of health accompanied or preceded by a corresponding change in its general appearance.

We have stated that the blood must be different as it flowed from the different organs because these organs are differently constructed, and appropriate very different parts of it for their nutrition or secretions. If any of these organs are altered by disease so that they will require different materials of the blood from what they required in health, it is evident the venous blood returning from them will contain different elements from what it contained in the healthy state of the organ. The venous blood returning from a healthy brain must be very different from that

returning from a brain softened by disease; the venous blood returning from a healthy skin must contain different effete matters from that returning from a skin covered with small-pox or erysipelas; the effete matters from a healthy condition of the whole system must be very different from those coming from a scrofulous, or syphilitic, or cancerous constitution. As far as the urine has been accurately and chemically investigated it has shown striking differences in these different diseases. Even its general appearance has been so much altered by different conditions of the system as to attract the attention of all observers from the earliest periods; but its chemical examination bids fair to become of high importance to physicians not only as a means of forming a more accurate diagnosis, but of indicating the most proper remedial treatment.

Prout has very fully described a condition of the system in which oxalic acid is developed in small quantities, probably much in the same way that sugar is formed in diabetes mellitus. This condition he has named the oxalic acid diathesis; it is sometimes accompanied by the formation of an oxalate of lime calculus, though this is by no means always the case, and sometimes by certain diseases of the skin which resist all treatment whatsoever until measures are taken to prevent the development of this acid in the system. Now the appearance and chemical qualities of the urine are points on which he mainly relies for his diagnosis of this diathesis. This, however, is only one instance of the importance of attending to this subject; there is no doubt when it has been fully investigated it will be found teeming with facts of the highest value to medical science. Of course the chemical examination of the urine can never take the place of the means at present employed for obtaining a knowledge of disease, but we cannot for a moment doubt that it may assist very materially in throwing light upon some obscure and fatal disorders of the general system, while in diseases of the kidneys it may be found hereafter to be as useful as the stethoscope in diseases of the chest.

The present treatise embraces every thing that is known in a chemical point of view in regard to the urine and all the sub-

stances found in it, and also the easiest and most approved modes of detecting them. The detailed accounts of all the ingredients will enable the physician, with only such general knowledge of chemistry as is given in a course of medical instruction, to separate them from the urine and study them. No difficulty whatever will be found in the application of the tests as prescribed in the part treating particularly of the examination of the urine. It is true there may be some difficulty in its quantitative analysis, which requires some apparatus and a knowledge of the first rudiments of analytical chemistry, but the present state of science is such that no one can hope to study Physiology or Pathology with success who has not first obtained this knowledge; those who have it we are confident will find the prescriptions sufficiently detailed to enable them to understand them thoroughly and to perform them.

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THE KIDNEYS.

THE kidneys are the organs which secrete the urine. They rest against the spine nearly in the middle of the abdomen. In man they are oval bodies about the size of the fist, and loosely covered in front by the peritoneum. By a transverse section they may be seen to be formed by two layers of different appearance. The *substantia corticalis*, or outer layer, seems to be composed of fine radiating fibres lying closely together; it consists in fact of infinitely fine interwoven tubes. Underneath this there is a layer having the appearance of a perfectly uniform mass, but consisting of microscopic tubes, which combine like radii into fewer and larger tubes, and hence has been called *substantia tubularis*. This layer terminates in mamillary prominences, *papillæ*, from which the urine exudes through numerous openings. Each of these *papillæ* is surrounded by a small sack, *calyx*, and these open into a larger sack, *pelvis*, which at a little distance

from the kidney contracts into a tube or narrow canal called the *ureter*, which empties into the bladder. The urine gradually collects in the latter as it exudes drop by drop from the papillæ, so that a large quantity can afterwards be evacuated at once. As extremes of the different forms of the kidney amongst mammalia it may be stated that in the whale (*cetacea*) each kidney is divided into about two hundred smaller ones, each of which has its papilla and calyx, while in beasts of prey and rodentia the kidney terminates in one papilla, the calyx of which forms the whole renal pelvis.

According to Jacobson the urine is secreted chiefly from venous blood in birds, amphibia, and fish; in web-footed birds the kidneys are larger in proportion to the size of the body, than in wading-birds, but larger in the latter than in birds of prey. In amphibia they generally consist of many smaller kidneys connected only by the common ureter. In fish they are larger in proportion to the rest of the body than in the foregoing classes of animals; they pass along the spine from the lowest part of the abdomen to the cranium; and are generally connected through their whole length. They evacuate the urine through the ureters from a common opening behind the anus. The ureter is often enlarged at a little distance above the opening. Jacobson has shown that the purple sack in snails must be an organ for the secretion of urine.

The examination of the parenchyma of the kidneys gives a better idea of the nature of such

structures than can be obtained from an examination of any other secreting organ. When we see broiled kidneys on our tables converted into a mass so hard that it may be cut with a knife, and feels firm to the teeth, we would easily suppose them to consist of a solid mass in which the secreting vessels were distributed. But this would be as erroneous as if we were to suppose the blood to be a solid body because it had been coagulated into a firm lump by heat; in fact the kidneys first acquire this firmness by cooking, whereby the albumen is coagulated, which in a soluble form, as in the brain, constitutes the chief ingredient of secreting organs. The secreting canals are here, as every where, surrounded by a capillary tissue in which we cannot discover any openings into the canals. In order to obtain a correct knowledge of the composition of the parenchyma of the kidneys it would be necessary to commence by expelling the fluids remaining in the arteries and capillary tissue.

I have attempted to replace the liquid contained in this tissue in the kidney of a horse, with distilled water, employing for this purpose hydraulic pressure on the artery, but without success, because when the vitality of these vessels ceases their capillarity presents an extremely great resistance; perhaps also certain manipulations were required which were unknown to me. I then stripped off the serous coat, cut the kidneys into thin slices, and suspended them in ice cold

water, which was renewed as often as it became discoloured. This emptied the larger blood-vessels. The kidneys were then bruised in a porcelain mortar with a wooden pestle, when the slices, to my great astonishment, were converted almost entirely into a liquid. Straining this through a linen cloth it did not pass through perfectly clear, and a fibrous mass remained on the cloth, which was tied up in linen and kneaded in pure water as long as it rendered it turbid. The soft solid animal matter which now remained formed only an extremely small portion of the volume of the kidney. It is true a certain portion of it had passed through the linen in a finely divided state, but even this was inconsiderable. Hence it is evident that the kidneys consisted of but a small mass of solid substance, which, as has been before represented, enclosed a large quantity of liquid. We have now to examine the properties of the solid matter, and of the liquid contained in it.

a. The residue on the cloth was colourless, fibrous, and could not be distinguished by its appearance from the fibrin of the blood. It became yellow and transparent by drying. Ether extracted a quantity of elain and stearin, with scarcely a trace of fatty acids. It easily softened in water and resumed its former appearance. It behaved chemically as follows:

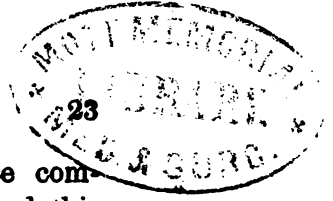
It shrivelled a little and became hard by long boiling; the water had scarcely dissolved any of

it. It was not soluble in concentrated sulphuric acid, nor was it decomposed, or gelatinized like fibrin. Nitric acid of 1.12 specific gravity dissolved it after moderate digestion, without decomposition of the acid; a few colourless flocculi only remaining undissolved. The solution was light yellow, becoming darker by saturation with caustic ammonia but without precipitation; neither was it precipitated by ferro-prussiate of potassa, nor by an infusion of galls. It was not attacked at first by concentrated chlorohydric acid, but it acquired gradually a dark violet colour, and dissolved after a few days without the assistance of heat. The solution was not made turbid by ferro-prussiate of potassa. Saturated with caustic ammonia, which produced no precipitate, and evaporated to dryness the animal matter dissolved with the sal ammoniac both in water and alcohol. It did not gelatinize with concentrated acetic acid, but by digestion with the dilute acid it separated into two substances, one of which dissolved in the acid, but the other retaining its form and appearance remained completely insoluble. The solution left a colourless, transparent residue when evaporated to dryness. Treated with a little cold water it dissolved, but became a jelly after 48 hours; this dissolved in a larger quantity of water, leaving a mucilaginous matter which likewise dissolved by gentle heat but precipitated again on cooling. The solution had no acid reaction, and was without colour, taste, or smell; it

was not precipitated by ferro-prussiate of potassa, by neutral, or basic acetate of lead, nor by bichloride of mercury; but on the other hand, it was precipitated by an infusion of galls in large, distinct flocculi, which did not agglutinate by heat. Caustic ammonia decomposed it in the same manner as acetic acid. What dissolved in ammonia remained colourless after evaporation, and contained a greater quantity of the matter soluble only in warm water, than the acetic acid solution, and also another matter insoluble in boiling water. The watery solution of the dry mass was without taste, and had neither acid nor alkaline reaction. Ferro-prussiate of potassa did not precipitate it even after the addition of an acid; but it was precipitated by neutral acetate of lead, bichloride of mercury, and tannin. The part insoluble in ammonia remained unchanged in appearance. It was almost insoluble in cold dilute caustic potassa, but by gentle digestion it dissolved slowly without colour and without residue. The addition of acetic acid in excess precipitated the portion insoluble in it, but retained the soluble portion. The precipitate remained insoluble in any excess of hot or cold acetic acid.

Hence it follows that the solid matter which constitutes the tissue of the kidneys is not fibrin, neither does it contain this substance, since it does not gelatinize with acids, and is not precipitated by ferro-prussiate of potassa. It is not composed of cellular tissue since it does not dissolve to glue.

THE KIDNEYS.



It resembles very closely the substance composing the fibrous coat of the arteries; and this circumstance seems to confirm the supposition that it is nothing else than a tissue of fine vessels.

b. The solution from the former solid matter was turbid, mucilaginous, and milky. Heated nearly to boiling, it coagulated almost to a solid mass, which required to be mixed with more water and to be boiled again before a complete separation of the coagulum from the liquid could be effected.

The coagulum was then well washed. When I attempted to extract fat from the moistened mass by ether, the albumen absorbed it and swelled up exactly as happens with albumen from eggs. It had therefore to be perfectly dried before it could be treated with ether. This then extracted a great deal of fat, consisting chiefly of fatty acids. On moistening the remainder with water, it resumed its former appearance. When dissolved in caustic potassa, and acetic acid added in great excess, part of the solid substance of the kidneys was precipitated, which had passed with the solution through the linen, and was insoluble in this acid. The coagulum was therefore composed of fat and albumen which mechanically enclosed the finely divided and suspended parts of the capillary tissue of the kidneys.

The solution from the coagulum was acid. By evaporation it afforded a yellow extract mixed with crystals. Alcohol of 0.833 extracted from it an

acid yellowish extractive matter with a content of chloride of sodium, and left by evaporation a residue which behaved exactly like a similarly obtained extract of flesh, which will be treated of hereafter. No trace of urea could be detected by nitric acid. The portion undissolved by alcohol was nearly all dissolved by water which, after evaporation, left a light yellow, transparent, hard mass, containing phosphates, and which gave a strong precipitate with lime water, and corresponded in every other respect with a similarly obtained solution of flesh. The part undissolved by water was soft, white, and slimy, it dissolved in warm water, and gave a precipitate with tannin.

These experiments show that the capillary vessels of the kidneys contain a highly albuminous liquid which is faintly acid from the presence of lactic acid. No fibrin seemed to be contained in this liquid, for if it had been present and coagulated after death in the vessels, it would have been dissolved in acetic acid and precipitated by ferroprussiate of potassa. As for the rest this solution contained the same dissolved substances as the solution from flesh, which were probably on their way to be evacuated with the urine.

I had expected to find urea in the solution from the kidneys, especially as Prevost and Dumas have endeavoured to prove that it is not formed in the kidneys, but merely evacuated by them; but nitric acid discovered no trace of it. Prevost and Dumas extracted the kidneys from living dogs,

cats, and rabbits, tied up the arteries and carefully healed the wound. The animals lived several days after this operation, eat as usual, but drank very little; they became sleepy and feverish on the sixth or ninth day, and finally died from the effects of the fever. Urea was found in the blood in sufficient quantity to be obtained in crystals and to be compared by analysis with that from the urine. The blood contained at the same time far more lactates and flesh-extract than usual. These experiments were afterwards repeated and confirmed by other physiologists. It appears to follow from them that urea as well as flesh-extract is formed in the body and only evacuated through the kidneys. But in this case it is difficult to conceive why it should not be present in the liquid from the kidneys, since the lactates and flesh-extract, which also occur in the urine, were both found in it; and it cannot easily be imagined that one ingredient would be evacuated sooner than another. I must here observe that Lecanu found urea in the liquid obtained by pressure, from the kidneys of a woman who had died suddenly after a fall. The liquid was filtered, evaporated to a syrup, treated with anhydrous alcohol, the solution evaporated, and the residue dissolved in three times its volume of nitric acid, previously deprived of nitrous acid, after which the agitated mass, at a temperature of 32° F., yielded granular crystals, which dissolved in water

and deposited by spontaneous evaporation a small quantity of nitrate of urea in plates.

The structure of the urinary passages resembles that of the intestines. The canals which lead from the kidneys to the bladder consist of a mucous membrane surrounded by cellular tissue, and covered exteriorly by the peritoneum. The bladder has a layer of muscular tissue between the mucous membrane and peritoneum which is attached to both membranes by cellular tissue. These muscular fibres are absent in some of the lower animals, in which the bladder consists merely of a dilatation of the ureters.

THE URINE.

ALL the waste matters which cannot be employed any farther in the system, together with those substances unfit for use which have been taken up by the absorbents of the skin and alimentary canal, are evacuated chiefly by the kidneys; the urine therefore may often contain, besides its ordinary ingredients, the accidental substances which are to be evacuated with it. Hence it is a very compound solution, and its nature is proportionally difficult to understand. It has been the object of research of many chemists. The first examination of it was by Van Helmont, whose results are to be found in his essay on calculous affections. Twenty-five years later, Brandt and Kunkle discovered phosphorus in the urine, which they obtained from its salts. Boyle afterwards made an analysis of it according to the time in which he lived. He also succeeded in obtaining phosphorus; he kept the preparation of it secret, and gave it to an apothecary in London for sale. The urine was examined about the same time

by Bellini, who found water, earths, and salts in it; and then by Boerhaave whose analysis is a masterpiece for his time. Marggraf showed that the phosphorus derives from the phosphates contained in the urine, and all efforts were then concentrated on these salts. Pott, Haupt, Schlosser, Schockwitz, Beyman, Klapproth, and others published essays on this subject. At last Rouelle Jr. directed his attention to the organic ingredients of the urine, and studied them particularly. He called them in general, soapy extract of the urine, but he could not effect their separation. He investigated the salts contained in the urine, compared human urine with that of herbivorous animals, and showed that the latter contained no phosphates but carbonate of lime and a substance resembling flowers of benzoin. Some years afterwards Scheele discovered that the urine contained phosphate of lime dissolved in excess of acid, and also lithic acid which was unknown before his time. The assertion that urine of very young children contained benzoic acid, has also been ascribed to him.* While the English che-

* This assertion of Scheele has been mentioned by Fourcroy in his treatise on benzoic acid in the urine of herbivorous animals. The truth is that Scheele asserted in his essay, on the acid of urinary calculi, that he also had found it in the urine of young children. But in his essay on the acids of fruits and berries, he mentions that in order to obtain oxalic acid, he treated concentrated urine (not mentioning that it was human,) with nitric acid; instead of oxalic acid he obtained an acid salt, resembling benzoic-salt. Was this nitrate of urea, or was the urine employed obtained from cattle? These are questions which cannot now be answered.

mist, Cruikshank, was engaged in the examination of diabetic urine, he instituted a comparison of it with urine in a healthy state and in different diseases. He thereby discovered crystallizable urea, and its precipitation by nitric acid; and he also gave a tolerably good method of ascertaining the relative quantity of certain ingredients in the urine. He showed that the composition of urine was altered in fever, dropsy, and dyspepsia; in fact our knowledge of the nature of urine may be dated from his work. His experiments were published in the year 1797, in Rollo's book on Diabetes Mellitus. Three years afterwards Fourcroy and Vauquelin described a detailed analysis of the urine; it is a very meritorious work, but in order to prevent the appearance of having appropriated any thing from Cruikshank's work, Fourcroy declares, in his *Système des Connoissances Chimiques*, that he and Vauquelin had known many years before the English chemist, the facts which form the most important part of the work of the latter. No one, however, can reproach Fourcroy for reserving for so long a time any other discovery which he could have published in his own name. Fourcroy and Vauquelin farther described the phenomena occasioned by putrefaction of the urine. Thénard afterwards showed that the free acid of the urine consists not only of phosphoric acid, but also of a combustible acid which he supposed to be acetic acid, but which shortly afterwards I ascertained to be lactic acid: and I also

showed that the urine contains an extractive matter, having a great resemblance to that in the liquids contained in flesh.

Urine considered in its average state, (for its proportion of water continually varies by increase or diminution of the perspiration,) has the following properties:—it is transparent, of an amber yellow colour, and a peculiar aromatic odour, which disappears by cooling, but reappears by heating it. It has an unpleasant, saline and bitter taste. It often becomes turbid on cooling, and deposits a gray or pale red precipitate, which is redissolved by heating it to 98° F. It has a distinct and strong acid reaction. Its specific gravity varies from 1.005 to 1.030. Prout considers 1.0125 as the average. In diseases it sometimes reaches a specific gravity as high as 1.050, but this is always an unfavourable sign.

When allowed to stand for a few days the urine becomes paler and exhales a weak ammoniacal odour, which is still urinous; it has an alkaline reaction, and becomes covered with a white slimy pellicle, in which, as well as on the inner side of the vessel, small white crystals are deposited. These consist of double phosphate of ammonia and magnesia. After some time the urine becomes so alkaline that it effervesces with acids, and is then applied for technical purposes as a weak solution of carbonate of ammonia. In the mean time it is concentrated by spontaneous evaporation and deposits at first yellow cubic crystals of sal ammo-

niac, and afterwards yellow octahædral crystals of chloride of sodium, and at last the microcosmic or fusible salt of the urine, which consists of double phosphate of ammonia and soda. The mother water is then an offensive brown syrup.

Urine does not coagulate by boiling; it yields by distillation an extremely offensive, colourless solution of carbonate of ammonia, which is formed during the ebullition. If distilled to dryness and the mass still further heated, it yields chloride of ammonium and empyreumatic oil with the carbonate and acetate of ammonia, and by strong heat a little phosphorus at last passes over.

Acids precipitate nothing from the urine at first, except oxalic acid which precipitates oxalate of lime; but when they are added in considerable quantity they develop a peculiar, sharp odour, resembling that of the fresh urine of a horse, and after some time they give it a darker colour. Alkalies produce cloudiness in the urine and precipitate earthy phosphate. Chloride of barium and nitrate of silver likewise produce a precipitate in the urine from the presence of sulphates and chlorides. Salts of lead precipitate sulphate and phosphate of lead. When the urine is neutralized by an alkali it is precipitated by the salts of zinc, tin, and mercury. The precipitate by the nitrate of mercury often assumes the same red colour which this salt produces on the epidermis, and derives from an animal matter which this precipitate, like the others, contains. With tannin it gives rather

a strong precipitate, when, as is sometimes the case, it contains albumen ; but this is no ordinary ingredient of the urine, and therefore tannin generally renders the urine but slightly turbid and does not deposit a precipitate till several hours have elapsed.

Fresh blood added to warm urine is at first coagulated, and then the colouring matter of the coagulum is dissolved in the free acids of the urine, which thereby becomes red.

The substances found in the urine are :—

a. The ordinary ingredients of the urine (in contra-distinction to the *accidental* which will be spoken of hereafter.)

1. *Mucus.* The mucus from the mucous membrane of the bladder mixes with the urine and passes off with it ; part of it is probably dissolved and imparts to it the property of forming a thick froth when shaken in its fresh state. The mucus passed off with the urine is seldom visible, because the refracting power of the two substances is nearly the same. If a person sits quietly for a few hours and then evacuates his urine into three glasses, so that it is divided into three equal portions, the first will contain the largest quantity of mucus, the second but little, and the third almost none, because the mucus has collected in the bottom of the bladder from which the urine is first evacuated. If the mucous portion be filtered while still warm, the mucus remains on the filter in separate, transparent, colourless lumps ; it then

shrinks on the paper, and at last forms a shining coat, like varnish. It does not resume its former appearance when moistened with water. It is not dissolved by sulphuric acid, but acetic and chlorhydric acids take up much of it, and their solutions are precipitated by ferro-prussiate of potassa. Caustic potassa dissolves it entirely. If a precipitate exists in the urine before evacuation, it mixes with the mucus, which loses its transparency on drying, and generally becomes milk-white. It can be freed from the admixture of the insoluble earthy salts by dissolving it in caustic potassa. If the mucus be not strained from the urine before it is cool, a quantity of small granular crystals may be seen in it when dry, which consist of lithate of ammonia, and which form even when the urine remains clear on cooling. They are not observed before drying. If two successively passed portions of urine are allowed to stand a few days these crystals will be observed to form in and on the mucus of the first portion, while there will be no deposition whatever in the second portion which contains no mucus.

2. *Lithic or Uric acid.* This ingredient of the urine was discovered by Scheele, who found that it formed the chief ingredient of several calculi analyzed by him, and he was thereby induced to search for it in the healthy urine of both adults and children. It exists in the urine of man and carnivorous animals, but not in that of herbivorous mammalia. It is of constant occurrence in other

orders of animals, even in the lowest. In some islands of the South Sea, it is found as a kind of half mineralized substance forming a superficial layer, and is called Guano, from the Indian word Huanu, which signifies dung. This layer has often a considerable thickness; it is formed from the dung of sea birds which are the sole inhabitants of these islands. The other ingredients of these excrements are gradually destroyed and the lithic acid remains in the form of a very impure lithate of ammonia.

Lithic acid may be procured in different ways. For instance by collecting the sediment formed in the urine by cooling, or by adding nitric or chlorohydric acid to the urine and collecting and washing the lithic acid gradually deposited; or from calculi consisting of this substance. But the easiest and most convenient way of obtaining it is from the white mass of lithic acid and lithates which are evacuated with the excrements of large serpents, and may be easily procured from the people who exhibit such animals. It may also be obtained from guano, and from the excrements of birds in general, especially the carnivorous, as the *corvis monedula*, which may be procured without much trouble from the high steeples where these birds roost in great numbers.

In all these substances lithic acid is more or less impure from admixture of foreign animal matters. They are to be first boiled with alcohol and afterwards treated with cold water till this

latter is no longer discoloured. The lithic acid from serpents may also be macerated with dilute chlorohydric acid, which extracts a considerable portion of phosphate of lime, and then washed with water, after which the impure lithic acid is dissolved in a dilute warm lye of caustic potassa, filtered from the insoluble residue, mixed with more caustic or carbonated potassa, and evaporated to a certain point, at which the lithate of potassa becomes insoluble in the alkaline solution, though this latter retains the animal matters dissolved. The whole becomes a thick paste on cooling. According to Braconnot, who is the author of this method, the cooled mass should then be transferred to a clean piece of linen cloth, the alkaline solution allowed to drain, the mass gently pressed, and then washed with ice-cold water or a solution of carbonate of potassa. Thus a moderately pure lithate of potassa is obtained.

The same may be effected by mixing the mass from which the lithic acid is to be extracted, after treatment with alcohol and water, with boiling hot water, to which, whilst constantly stirred, a lye of caustic potassa is added in quantity exactly sufficient to dissolve the lithic acid, after which the boiling hot solution is to be filtered and cooled. A tolerably pure lithate of potassa then precipitates, which is to be washed on a filter with cold water and pressed. The mother and washwaters yield by evaporation more, but impurer

salt, which after subsequent solution in boiling water precipitates pure.

According to Wöhler an impure lithic acid may be rendered pure by dissolving it in caustic potassa and mixing the solution with a solution of sal ammoniac as long as a precipitate is formed. All the lithic acid precipitates as lithate of ammonia in the form of an almost transparent jelly which gradually subsides to a perfectly white powder. Very dilute solutions should be employed, because otherwise the whole coagulates to a stiff jelly. If the sal ammoniac has been employed in excess and both the solutions mixed while hot, no lithic acid remains in the solution, especially when it has been heated to expel all the ammonia that was liberated.

The lithic acid is obtained from the purified lithate of potassa by decomposition with chlorohydric acid. This can be effected best by pouring the boiling solution of the salt of potassa into the chlorohydric acid, for otherwise the lithic acid is apt to retain some potassa. The precipitate is at first gelatinous but is gradually converted into small, white, shining scales which should be well washed with cold water.

Henry prescribes the purification of lithic acid by digestion with carbonate of ammonia, which he thinks dissolves all the animal matters; but this is a very uncertain method, not to mention that the residue is lithate of ammonia which must

be freed from ammonia by digestion with chlorohydric acid, a circumstance which Henry does not mention.

Fritzsche recommends the following method of purification. Excrements of serpents or lithic acid calculi are to be dissolved in warm concentrated sulphuric acid, the clear, generally brown coloured, solution is to be decanted while still hot and mixed while agitated with small portions of water as long as it effects a precipitate. The lithic acid then precipitates in dazzling white crystals and quickly subsides so that the acid solution may be decanted. The precipitate is then filtered and washed at first with sulphuric acid of about the same dilution as the decanted liquid and afterwards with water. This is necessary, because if the remaining mother liquid were removed from the lithic acid by washing with water, the brown decanted liquor which does not separate any lithic acid by water will, by still greater dilution, yield a precipitate of dissolved animal matters and would cause an admixture of these in the lithic acid precipitated by the wash-water.

Lithic acid obtained in the above way has the following properties: it forms white crystalline scales which are soft to the touch; it has neither taste nor odour, reddens moistened litmus paper when laid on it, and requires according to Prout more than 10,000 times its weight of cold water, but rather less of boiling water for its solution.

Henry states that it requires 1720 parts of cold, and 1400 parts of boiling water to dissolve it; but his lithic acid seems to have been bilithate of ammonia. According to Mitscherlich it requires 10,000 parts of cold water for solution. Its solution in boiling water reddens litmus paper. It is insoluble in alcohol and ether. It is decomposed by dry distillation; it first sublimes carbonate of ammonia in solid form, then yields a large portion of cyanhydric acid and brown empyreumatic oil, and at last a crystalline mass which Scheele had observed and compared to benzoic acid, and which forms seven-fifteenths of the weight of the lithic acid. Chevallier and Lassaigne afterwards described it as a peculiar acid and called it pyro-lithic acid; at last Wöhler showed that it was cyanuric acid. According to him the sublimate from the distillation of lithic acid contains a considerable quantity of urea combined with cyanuric acid, as was afterwards proved by Kodweiss. According to Henry carbon remains in the retort to the amount of one-sixth of the acid. Lithic acid chars without fusion when heated in an open vessel. The carbon afterwards burns with difficulty and leaves no residue. When heated in the open air lithic acid is characterized by the strong odour of prussic acid which it generates, and at last, also, by the acid odour of cyanic acid.

Moistened lithic acid swells up in chlorine, generates, according to Liebig, carbonic acid and cyanic acid, and is converted into oxalic acid and

sal-ammoniac. It does not change in dry chlorine at ordinary temperatures. But if the perfectly dry acid be heated in perfectly dry gas it yields according to Liebig, a large quantity of cyanic and chlorohydric acid, and, according to Kodweiss, also solid chloride of cyanogen. It thereby disappears except a small carbonaceous residue. Chlorine-water and nitric acid form oxalic acid by long continued digestion with it. Nitric acid produces by its action a long series of important compounds which will be mentioned in another place. I will here only mention that lithic acid dissolves with effervescence even in a very dilute warm nitric acid, and that when this solution is evaporated to dryness by a gentle heat a red residue remains which is soluble in water without colour. This reaction is used as a test for lithic acid. It is soluble in small quantity in concentrated sulphuric acid, but if the latter be hot a larger quantity is dissolved without decomposition if the temperature be not raised too high. It again precipitates by the addition of water. We have seen that Fritzsche's method of purification consisted in this. But he has also discovered a chemical combination of lithic acid with sulphuric acid, which is obtained by dissolving it in warm concentrated sulphuric acid and decanting the clear warm solution from which the sulphate of the lithic acid separates in large well defined colourless crystals. Purified lithic acid is not necessary for this purpose; that which separates

from the brown acid solution of an impure lithic acid is pure and colourless. These crystals melt at 158° F., and solidify again to a crystalline mass when the temperature is reduced. At 302° F. they begin to be decomposed. The combination attracts moisture from the air and is converted into a mixture of dilute sulphuric acid and precipitated lithic acid. Water decomposes it in a similar manner. According to Fritzsche's analysis the crystals consist of one atom of lithic acid, four atoms of sulphuric acid, and four atoms of water.

Lithic acid has been analyzed by Berard, Prout, Döbereiner, Göbell, Kodweiss, Mitscherlich, and Liebig. The results of the latter two agree, and are near to that of Prout. I will here give the results of the analysis by Mitscherlich and Liebig:

| | Liebig. | Mitscherlich. | Atoms. | By Calculation. |
|---------------|---------|---------------|--------|-----------------|
| Carbon..... | 36.063 | 35.62 | 5 | 36.00 |
| Hydrogen..... | 2.441 | 2.38 | 2 | 2.36 |
| Nitrogen..... | 33.361 | 34.60 | 2 | 33.37 |
| Oxygen..... | 28.126 | 27.20 | 3 | 28.27 |

Its atomic weight is 1061.216. It is the oxide of a radical whose composition is expressed by $C^5 H^3 N^2$; and of which we will find a substance in urinary calculi with a lower degree of oxidation. Lithic acid is then $C^5 H^3 N^2 + 3O$, and the lower oxide $C^5 H^3 N^2 + 2O$.

Several chemists double the numbers of atoms of its elements, and therefore, also its atomic weight; for the reason that lithic acid is a weak

acid, and like boracic acid and the fatty acids, principally forms acid salts, while the neutral salts are decomposed by water when the base is soluble in it, leaving an insoluble bilithate.

Lithic acid expels carbonic acid with difficulty from the alkaline carbonates, forming a bicarbonate and a bilithate. According to Wetzlar if a solution of carbonate of potassa or soda contains one-twelfth of its weight of the carbonate, the acid precipitates with a portion of the alkali and thereby converts another part into bicarbonate which remains in the solution. But if the content of the carbonate is only a half per cent. the lithic acid dissolves rather easily, because an excess of alkali in the solution diminishes the solubility of the lithate in proportion as the solution becomes concentrated. For the same reason lithic acid dissolves in a solution of borax, but the borate which is formed prevents the solubility of the lithate less than the carbonates. Hence lithic acid is far more soluble in borax. Most of the neutral lithates dissolve with difficulty in cold water and form white, earthy, tasteless powders. By dry distillation they char without fusion and yield carbonate of ammonia, cyanide of ammonium, empyreumatic oil, many of them also yield cyanic acid, and those with fixed alkaline bases leave a soluble cyanide.

Lithate of potassa is obtained by dissolving lithic acid in a warm lye of caustic potassa till it is perfectly saturated. The salt is deposited on

cooling in small crystalline grains. When cooled very slowly it crystallizes in fine scales. It requires 480 parts of cold water for solution but much less of hot water. A slight excess of potassa renders it still much more soluble in boiling water, but a neutral salt then deposits on cooling. A greater excess of caustic potassa in the solution considerably increases the solubility of the salt even at ordinary temperatures, but a still greater excess diminishes it again; hence the salt is deposited by concentration of the solution. From the solution in caustic potassa carbonic acid precipitates probably a neutral salt in the form of a very voluminous jelly. Carbonate of ammonia also precipitates it; the carbonic acid combines with the potassa which thereby loses its power of dissolving the salt; this precipitate contains also lithate of ammonia. The dry distillation of lithate of potassa yields much cyanide of potassium. According to Gay-Lussac lithic acid when fused with caustic potassa is converted into oxalic acid, with development of ammonia.

Lithate of soda behaves like the salt of potassa. It is contained in small quantity in the urine, and also forms the earthy concretions which occur in gout.

Lithate of ammonia resembles the foregoing salts and has about the same solubility in water. It may be distinguished from them by its burning without residue, and generating ammonia with potassa. The bases of these alkaline lithates are recognised by extracting them with chlorohydric

acid, evaporating the solution, and examining whether the chloride of sodium, potassium, or ammonium is obtained. According to Coindet's experiments, lithic acid is contained in the urine of birds, as bilithate of ammonia, which likewise forms a white earthy powder. The urine of serpents seems to consist of the same salt, at least their excrements generate with potassa a considerable quantity of ammonia. Lithate of ammonia may be obtained either by direct combination or by precipitation of lithate of potassa by sal-ammoniac. When freshly precipitated it forms a transparent, stiff jelly, which soon collects to a light, white powder.

Nothing more is known of the other lithates than that the combinations of this acid with the alkaline earths have about the same solubility in cold water as the foregoing salts, so that, for instance, when lime water is saturated with lithic acid the salt formed with the lime remains in solution. If a warm saturated solution of lithate of potassa be mixed with a solution of any of these earthy salts they are thereby precipitated, but the salt of magnesia less so than the others, because its lithate is more soluble. Henry was the first to observe this, and was led to the fortunate experiment of using magnesia for preventing lithic acid sediments in the urine. A solution of lithate of potassa is precipitated by the salts of all the earths proper and metallic oxides. The chloride of gold only forms an exception; after some time it ac-

quires a violet colour. *Lithate of mercury* is obtained, according to Wöhler, by mixing a solution of chloride of mercury with a solution of neutral lithate of potassa. It forms a white powder, but has a pale yellow colour when completely dry. It does not seem to be decomposed by boiling with potassa. By heat it assumes a transient lemon colour. By stronger heat it blackens and yields, besides mercury, much cyanic and cyanohydric acid, but neither empyreumatic oil nor water. Carbon remains in the retort. Urea also is probably formed. The gases burn with a violet colour.

Lithic acid in the urine. Warm urine contains far more lithic acid in solution than can be dissolved in an equal volume of boiling water. From this fact Prout was induced to suppose that lithic acid was dissolved in the urine as lithate of ammonia, which was decomposed on cooling by the other free acids. It is not easy to say how a liquid of such complicated composition as the urine may retain the insoluble matters in solution. It may be possible that the lithic acid at the temperature of the body counteracts the phosphoric and lactic acids in their acid salts, but this is probably not the case. We know also that, for instance, iodine will dissolve in larger quantity in water containing chloride of sodium or ammonium in solution, than in pure water, although no combination of these salts with iodine is known. Be this as it may, the lithic acid precipitating from urine

on cooling, is in a free state, with so small traces of ammonia and soda, that they are not worth notice, especially when the mucus has been separated by filtration before cooling. The precipitate is at first pulverulent and gray like clay, but as it gradually collects becomes of a pale pink colour, and crystalline and scaly when dried. The finer the scales are the purer is the acid, and on the contrary, the more distinctly the crystals can be seen in it the more impure it is from a content of bases. The fine scaly precipitate dissolves in caustic potassa without any odour of ammonia; a trace of it may, however, be discovered by holding over it a glass rod moistened with muriatic acid, and a trace of carbonate of soda remains when it is burned on platinum foil. If on the other hand such sediment be crystalline and consist of small red angular crystals, it then generates ammonia with caustic potassa in a perceptible quantity, and the solution which was red at first becomes yellow afterwards. It also leaves after ignition on platinum foil a large quantity of ashes. Lithate of ammonia rarely precipitates from the urine on cooling. When this happens it subsides but slowly, and dissolves again when it is washed with water. It generally either crystallizes after twenty-four or thirty-six hours from urine depositing no sediment, or the scaly acid already precipitated alters, by remaining in urine becoming alkaline, into large reddish granular crystals of bilithate of ammonia. The mucus wherein the lithic acid is deposited takes so considerable a part in this formation of an

ammoniacal salt, that if urine be filtered after commencing cloudiness, the precipitate on the filter washed, and then left under water, the crystallization will often take place in a few hours. The sediment from urine filtered while still warm, retains, after washing and drying, its glittering, fine, scaly appearance; while on the contrary, the sediment from unfiltered urine is distinctly crystalline and ammoniacal after it has been washed and dried.

All the lithic acid does not precipitate from the urine on cooling, but a considerable portion of it remains in solution. Nor does every healthy urine deposit a sediment on cooling, at least not at the warmer temperatures of the air. If filtered urine is evaporated, it deposits a gray sediment consisting of a mixture of lithic acid and phosphate of lime. The lithic acid may also be precipitated, as already stated, by a large addition of nitric or chlorohydric acid to the urine. It then deposits, generally after some time, either as powder or as crystals according to the rapidity with which it precipitates.

The lithic acid precipitated from urine frequently acquires after washing, a pink or brick colour, although it appeared gray while it remained in the urine. This colour is derived from a foreign colouring matter combined with the acid. In intermittent fever the intensity of this red colour considerably increases; the urine deposits after every paroxysm a strong lateritious, or pink, or bright carmine precipitate. This colouring matter

was first examined by Prevost, who considered it a peculiar acid which he called *rosacic acid*, but he afterwards observed that it was nothing else than a combination of lithic acid with a peculiar extractive red colouring matter. This colouring matter is dissolved when the red precipitate from the urine of a fever-patient is treated with boiling water or boiling alcohol. After evaporation the alcoholic solution leaves a scarlet powder without taste or smell. Vogel states the following particulars. The colouring matter extracted by alcohol still retains a portion of lithic acid. It does not exhale the odour of burnt horn by ignition. It is soluble with a pink colour in sulphuric acid, which soon becomes dark red; water precipitates lithic acid unaltered. Sulphuric acid diluted with three parts of water extracts the colour and becomes red, but leaves the lithic acid behind. Liquid sulphurous acid turns it carmine. Nitric acid and chlorine produce the same change with it as with pure lithic acid. Chlorohydric acid gradually destroys the red, and converts it into a yellow colour. It is dissolved by alkalies. The solution soon becomes yellow and behaves exactly as a solution of lithic acid in an alkali. Duvernoy states that the red sediment in fever may be produced from ordinary urine by evaporating it to one-third or one-fourth, and then mixing it with a little nitric acid and permitting it to stand for 12 or 16 hours, whereby it gradually becomes dark-red. If then a lithate be added lithic acid precipitates of

a red colour, and alcohol extracts from it the ordinary red precipitate. When a solution of the red matter in water is mixed with a solution of acetate of lead, a pale pink precipitate is formed. By nitrate of silver it becomes green in a few hours. Fromherz and Gugert who examined the red coloured sediment from the urine of a person affected with a liver complaint obtained the same results. By long digestion in water or boiling with alcohol, a red extractive colouring matter was obtained, which was coloured yellow by alkalies. Its property of reddening litmus was due only to its colour.

On the other hand Prout ascribes the red colour in the sediment of the urine to an admixture of purpurate of ammonia, because the purpuric acid may be artificially produced by treating lithic acid with nitric acid; and he found nitric acid in unknown combination in the precipitate from urine in fever. He digested the precipitate with hydrate of baryta and water, filtered the solution, precipitated it exactly with sulphate of potassa, evaporated it, and obtained after sufficient concentration, crystals of nitrate of potassa. Nitric acid however occurs so very rarely that Wurzer found it but once in eleven cases examined by him with this view. The solubility of this colouring matter in alcohol, which is not coloured by purpurate of ammonia, is against the assumption that the colour derives from purpurate of ammonia. It is certain that when lithate

of ammonia is mixed with a solution of purpurate of ammonia in acetic acid, which does not destroy its colour, the lithic acid precipitates with a pale pink colour, exactly like the precipitate from the urine. But boiling alcohol extracts no trace of a colouring matter. I tried the experiment of mixing urine with the above mentioned acid solution of a purpurate, while I left another portion of the same urine unmixed. Both deposited a sediment perfectly alike as regards the colour, and by both, boiling alcohol became yellow, without the addition of the purpurate at all increasing the colour of the precipitate, or seeming to impart to it any of its colouring matter, since both became yellow after boiling.

The ordinary pink precipitate which frequently deposits even from healthy urine does not appear to agree perfectly with that in fever, since water extracts nothing from it, and alcohol, when long boiled with it, becomes yellow and leaves after evaporation a dark orange coloured extractive residue which dissolves with difficulty in water, leaving the red pulverulent colouring matter behind, and consists of lithate of soda with a little lithate of ammonia. A small portion of alcohol extracts the red colouring matter from the red powder soluble in much water, and leaves a yellow pulverulent lithic acid. The acid boiled with alcohol does not become colourless but yellow, and acetic acid extracts part of the yellow colour.

3. *Lactic acid.* This acid is a common product

of the spontaneous decomposition of animal matters within the body; it is therefore contained in all its liquids. It forms most abundantly in the muscular tissues, is saturated in the blood by its alkali, and again separated from it with acid urine by the kidneys. This is the principal of the free acids of the urine; and although the urine contains biphosphates of ammonia and lime, they are only formed by the lactic acid dividing the bases with the phosphoric acid.

By an examination of the urine performed by me in the year 1807, I discovered the presence of this acid,* which had not until then been considered an ingredient of this secretion, and as many chemists presumed, without good reasons, that this acid was acetic acid, I instituted a new examination of it, the result of which was that lactic acid could not be considered acetic acid.†

The great number of substances contained in the urine render the separation of the lactic acid in its pure state very difficult, but it is not difficult to obtain it sufficiently pure to be recognised. By my first experiments on this subject the residue from the evaporated urine was extracted by alcohol of 0·833, the alcohol distilled in a water bath, the extract dissolved in water, mixed with a large quantity of hydrate of lime and boiled as long as ammoniacal odour indicated the existence of unde-

* *Föreläsningar i Djurkemién.* Stockholm, 1806, II. p. 287.

† *Ibid.* p. 430.

composed urea. The lime became brownish-yellow from the destruction of animal matter. The almost colourless solution was filtered, evaporated to dryness, dissolved in spirits of 0.845, and mixed drop by drop with sulphuric acid diluted with but little water, as long as any sulphate precipitated. The acid solution which now contained the added excess of sulphuric acid and chlorohydric acid, was digested with newly precipitated carbonate of lead until it was impregnated with lead, then filtered and evaporated till all the alcohol was volatilized. The residue was then digested with oxide of lead and water, whereby the lactate of lead was converted into an insoluble basic salt, which was separated from the supernatant liquid, washed with a little water, and decomposed by sulphuretted hydrogen, whereby the lactic acid was set free and remained after evaporation in the form of a yellow acid syrup which did not become dry by heat, but became more dilute by standing in the open air. But after saturation with a base it always showed distinctly an admixture of the extractive ingredients of the urine.

Alcohol does not extract all the lactic acid from the residue of the urine; a small portion of it remains undissolved, probably retained by the animal matters; but if the free acid contained in the insoluble residue be saturated with ammonia, alcohol will then extract lactate of ammonia from it.

The lactic acid contained in the urine is the principal solvent for the phosphate of lime con-

tained in it also, which may be easily shown by extracting the free lactic acid with alcohol from inspissated urine and adding water to the residue, when it will be found that the greatest part of the phosphate of lime remains undissolved.

4. *Other organic acids.* Many chemists, especially Proust and Thénard, assume a content of acetic acid in the urine. The former stated that when urine was mixed with so much sulphuric acid as to decompose all its salts, and then distilled, a water passed over containing a great deal of acetic acid. This he gave as the most important proof of the presence of this acid in the urine. I have repeated this experiment, but with different results from what I expected after Proust's statement. By mixing urine with sulphuric acid it acquires a very disagreeable, though peculiar and characteristic odour. A colourless liquid then passed over by distillation, which had a very offensive odour of putrid urine. I continued the distillation until about one-tenth of the original volume of the urine remained. The distillate reddened litmus paper, but had no observable acid taste, and made hardly any other impression than by its smell. It was strongly precipitated by acetate of lead, lime water, barytic water, and nitrate of silver; the latter precipitate was not soluble in nitric acid. It was saturated with so much hydrate of baryta as to become alkaline; which produced a voluminous precipitate, proving on examination to be carbonate of baryta. The car-

bonic acid derived from the decomposition of urea into carbonate of ammonia, the ammonia of which was retained by sulphuric acid. By evaporating the filtered barytic solution it long retained the odour of the volatile substance produced by the distillation, and there at last remained a small syrupy residue which solidified, in a dry and warm place, into an irregularly crystalline saline mass, with a barytic taste. In order to test it for acetic acid it was mixed with some sulphuric acid, whereby butyric acid was generated in considerable quantity; by the addition of more sulphuric acid the odour became pungent and might have been mistaken for that of acetic acid concealed by butyric acid, if the precipitate by nitrate of silver had not indicated that it came from chlorohydric acid. This experiment therefore shows that by distillation of urine with sulphuric acid, no observable quantity of acetic acid is produced, and therefore it cannot be contained in urine either in a free or combined state. But on the contrary it proves the presence of a certain quantity of butyric acid. But since this acid has only been found in the urine of a single individual it remains undetermined at present whether it exists as a constant or merely as an accidental ingredient in the urine.

It has also been stated by chemists that benzoic acid exists in the urine of young children and herbivorous animals. Rouelle found that chlorohydric acid precipitated an acid salt from the concentrated urine of a cow, which he compared to

benzoic acid. This result was afterwards confirmed by Fourcroy and Vauquelin, and for this reason benzoic acid has generally been assumed to be an ingredient in the urine of cows and horses. Liebig afterwards found that the acid obtained from the urine by Fourcroy's prescription in fact resembled benzoic acid, and under certain circumstances could be converted into it, but that it had a different composition and other properties than benzoic acid; hence he named it *hippuric acid*. Still later experiments have shown that the urine of these animals sometimes contain benzoic acid, though much less frequently than hippuric acid. This has in fact been found by Dumas, Liebig, and Erdmann. Liebig considered it probable that benzoic acid was the product of the evaporation by boiling, and that it derived from the decomposition of hippuric acid. Erdmann on the contrary, found that the urine of horses by similar evaporation yielded sometimes benzoic acid, and sometimes hippuric acid; and mentions as a proof that the presence of benzoic acid does not depend on such an accidental circumstance, that both acids never occur together, but either only benzoic or only hippuric acid. Both of these acids may therefore be considered as ingredients in the urine of herbivorous animals. Since benzoic acid has already been described in the vegetable chemistry I will here only treat of hippuric acid.

Hippuric acid. This acid occurs in the urine partly combined with urea and partly with soda.

After evaporating the urine to one-eighth or less, it is mixed with chlorohydric acid, which after some time forms a yellow brown crystalline precipitate. This should be dissolved, according to Liebig, in a mixture of hydrate of potassa and water, the solution heated to boiling, and a solution of hypochlorite of lime added by drops until the urinary odour disappears; it is afterwards digested with animal charcoal until it becomes colourless, filtered while hot, mixed with chlorohydric acid until it acquires an acid taste and then slowly cooled, whereby the acid separates in long colourless needle shaped crystals. Dumas rejects the use of hypochlorite of lime for purifying the acid, stating that it decomposes the hippuric acid; but experiments both by Erdmann and Fehling have shown that this is not the case when the hypochlorite is not added in great excess.

When larger quantities of hippuric acid are prepared it is obtained in transparent, four-sided prisms two or three inches in length, which are terminated by two oblique surfaces. It has almost no taste or is only feebly bitter, but it strongly reddens moistened litmus paper. By gentle heat it melts to a colourless liquid and congeals again by cooling into a crystalline mass. By this fusion it soon enters into decomposition, the upper surface becoming brownish-yellow, which colour soon spreads through the whole mass. Exposed in a retort to a gradually increasing heat, a portion of it sublimes colourless and crystalline, and this sublimate consists of benzoic acid and benzoate of

ammonia. A liquid matter afterwards passes over in red drops which solidify and retain their transparency. The mass thereby acquires a pleasant odour like that of tonka bean. The red substance is resinous, insoluble in water, but soluble in alcohol and ammonia, after the evaporation of which it remains as an uncrystalline mass. The residue in the retort is black, generates cyanhydric acid by ignition and leaves a porous coal. This generation of cyanhydric acid had already been observed by Vogel. In vacuo the products of distillation are the same, except that towards the end of the operation gaseous matters are generated which cause the guage of the air pump to rise.

Hippuric acid has nearly the same solubility in cold water as benzoic acid. A warm saturated solution cooled to 50° F. and allowed to deposit what it will, contains in one thousand parts of water only 2.66 parts of hippuric acid. It is far more soluble in boiling water. On cooling it separates in distinct crystals without forming like benzoic acid an aggregation of microscopic crystals in which the water is included. It is much more soluble in alcohol than in water. It is sparingly soluble in ether, and equally in cold and warm ether. The acid remains crystalline from both solvents after evaporation. The crystals of hippuric acid contain no water of crystallization, and give no trace of it either by fusion or by destructive distillation. It is dissolved by sulphuric acid at 248° F. without becoming black; it is again pre-

cipitated by the addition of water. By stronger heat the solution is decomposed and sublimes benzoic acid. Concentrated nitric acid dissolves it by boiling, without effervescence. Liebig found that it was hereby converted into benzoic acid. By experiments performed by me on this subject, and in which the excess of nitric acid was evaporated by boiling until a small quantity of the solution remained, hippuric acid could be precipitated from this solution by water, which did not seem to be altered; but the nitric acid employed by me had originally only a specific gravity of 1.26. Chlorohydric acid dissolves hippuric acid by heat without alteration, and deposits it in crystals on cooling. It is decomposed by continued boiling with a great excess of hypochlorite of lime.

Crystallized hippuric acid has been analyzed by Liebig, Dumas, and Mitscherlich with the following results:—

| | Liebig. | Dumas. | Mitscherlich. | Atoms. | By Calculation. |
|----------|----------|---------|---------------|----------|-----------------|
| Carbon | . 60.742 | .. 60.5 | ... 60.63 | 18 | 60.76 |
| Hydrogen | 4.959 | .. 4.9 | ... 4.98 | 9 | 4.92 |
| Nitrogen | 7.616 | .. 7.7 | ... 7.90 | 1 | 7.82 |
| Oxygen | . 26.483 | .. 26.9 | ... 26.49 | 6 | 26.50 |

Although so far as I know no experiments have been made to prove that it contains one atom of water, yet this has been reasonably assumed to be the case. The acid consists then of $C^{18} H^{18} N^1 O^5 + HO$. The atomic weight of the anhydrous acid is 2152.755, and its capacity 4.645 or one fifth of

its content of oxygen. In its anhydrous state it consists of

| | Atoms. | By Calculation. |
|----------------|--------------|-----------------|
| Carbon . . . | 18 | 63·913 |
| Hydrogen . . . | 8 | 4·638 |
| Nitrogen . . . | 1 | 8·224 |
| Oxygen . . . | 5 | 23·225 |

The facility with which this acid can be converted into benzoic acid by dry distillation, gave rise to the supposition that it is a combination of benzoic acid with an azotic organic oxide, and therefore analogous to indigo-sulphuric acid in so far as it combines with bases without separation of the oxide. Considered with this view it might consist of one atom of benzoic acid $C^4 H^5 O^3$, and one atom of an organic oxide $C^4 H^4 N^1 + 2O$. I therefore proposed to alter the name of hippuric acid, (from *ἵππος*, a horse) which did not seem proper to me since it is also contained in the urine of other herbivorous animals, into urine-benzoic acid. But since experiments to be mentioned presently seem to prove that it contains no benzoic acid, I have again abandoned this name.

Starting with a similar view, Pelouze afterwards endeavoured to render it probable that this acid contains formic acid in chemical combination with the cyanohydrate of the oil of bitter almonds, which does not separate by saturation with bases. The following diagram represents Pelouze's view:—

| | | |
|---------------------------------------|--------------------|------|
| 1 atom of bitter almond oil | 14C + 6H | + 20 |
| 1 " cyanohydric acid | 2C + 1H + 1N | |
| 1 " formic acid | 2C + 1H | + 30 |
| <hr/> | | |
| 1 atom of anhydrous hippuric acid . . | 18C + 8H + 1N + 5O | |

In support of this view Pelouze states that if hippuric acid be digested with dilute sulphuric acid and hyperoxide of manganese, it generates carbonic acid gas, and if the solution be filtered while hot, benzoic acid separates in such large quantities that Pelouze considers this the cheapest method of preparing this acid. The solution contains besides the sulphate of manganese a portion of the sulphate of ammonia. According to Pelouze's view formic and cyanohydric acids were decomposed with the formation of carbonic acid and ammonia, while the bitter almond oil is oxidized to benzoic acid.

If this view were correct, the same products should be obtained by the influence of other oxidizing reagents. But Fehling has shown that when sulphuric acid is boiled with water and hyperoxide of lead, part of the acid is destroyed, while another portion is saturated by the resulting protoxide of lead. Carbonic acid is generated during the ebullition, hippurate of lead crystallizes on cooling, and the filtered solution yields benzamid by evaporation, which Fehling found to be identical both in appearance and composition with benzamid obtained in the ordinary way. The hippuric acid in the obtained salt of lead yielded after separation from the oxide of lead, the same products when treated in the same manner. Fehling concluded from these experiments that the acid in hippuric acid was one of the acids which consist of $C^4 H^1 O^3$ (for instance malic,

pyromalic, fumaric or aconitic acid) combined with benzamid in such manner that it cannot be separated by saturation with bases. If then

$$\begin{array}{r}
 \text{from one atom of hippuric acid} = 18\text{C} + 8\text{H} + 1\text{N} + 5\text{O} \\
 \text{be deducted one atom benzamid} = 14\text{C} + 7\text{H} + 1\text{N} + 2\text{O} \\
 \hline
 \text{the acid remains} = 4\text{C} + 1\text{H} \qquad + 3\text{O}
 \end{array}$$

which acid he supposes to be converted by the excess of oxygen in the hyperoxide of lead into carbonic acid and water, whereby the benzamid is set free. These interesting metamorphoses show that the elements of hippuric acid have a great tendency to form combinations of the radical of benzoic acid $=\text{C}^{14} \text{H}^5$, and the re-action with hyperoxide of lead shows also that the benzoic acid is not contained in it already formed, since it is difficult to conceive that the already formed benzoic acid $\text{C}^{14} \text{H}^5 \text{O}^3$ should be reduced by the hyperoxide of lead to $\text{C}^{14} \text{H}^5 \text{O}^2$, which substance is supposed to be combined in benzamid with N H^2 . However well these metamorphoses agree with the supposed composition of hippuric acid, yet they afford no certain proof that this acid has in reality such a complex composition. In the meanwhile it may be more correct to consider hippuric acid as consisting simply of $\text{C}^{18} \text{H}^8 \text{N} + 5\text{O}$ or of one atom of an organic ternary radical and five atoms of oxygen, and this so much the more because the compound organic acids, which consist of an organic acid combined in such a manner with an organic oxide that this latter can-

not be separated from the acid by bases, generally contain a large number of atoms of oxygen. The hippurates have a bitter taste almost like the salts of magnesia. By dry distillation they yield an empyreumatic oil which has the smell of hay, and a small quantity of alkaline water. Even the empyreumatic oil restores the blue colour of reddened litmus paper. I will not decide whether this is due to a content of ammonia, or whether this oil belongs to the same class of bases as the substances found in other empyreumatic oils, which may possibly be the case.

Hippurate of potassa dissolves very easily in water and crystallizes from a syrupy solution in lamina like acetate of potassa. The *soda salt* crystallizes from a less concentrated solution. The *hippurate of ammonia* crystallizes like the hippurate of potassa, but the crystallized salt reddens litmus paper. According to Liebig they become pink by fusion and leave a red acid, which after solution yields red crystals, which otherwise behave like hippuric acid. The *hippurates of baryta and strontia* crystallize in white transparent lamina. With an excess of base they form a rather insoluble salt which when concentrated by boiling gelatinizes and on cooling deposits as a porcelain-like mass. Evaporated in vacuo and fused it remains transparent after solidification. The *hippurate of lime* crystallizes during evaporation in broad plates and on cooling in rhombohedrons. It contains no water of crystallization

and is soluble in 18 parts of cold and 6 parts of boiling water. The *hippurate of magnesia* is easily soluble, and crystallizes with difficulty. The *hippurate of alumina* is soluble in water. The *hippurate of lead* has about the same solubility in water as the acid itself, and can therefore be best obtained by mixing hot solutions of hippurate of potassa and acetate of lead. It crystallizes in broad, laminated, soft crystals of pearly lustre. A boiling saturated solution is converted by cooling into an aggregation of crystals from which the water may be removed by pressure. According to Liebig the crystals become opaque and white in the air; they contain water of crystallization. It is also soluble in alcohol. By digestion it dissolves more oxide of lead. The basic salt is rather insoluble. By evaporation of its boiling saturated solution it becomes covered by a coherent shining pellicle, and afterwards the whole solidifies to a white mass. The oxide of lead digested with the hippurate of lead forms a coherent mass, which while yet under the water, is apt to blacken and become scorched. The *hippurate of cobalt* crystallizes in pink needles, which contain water of crystallization. The *hippurate of copper* forms also deep blue, needle shaped crystals, containing water of crystallization. Hippuric acid forms soluble salts with the oxides of *nickel, manganese, and mercury*.

It is believed that hippuric acid has also been found in the urine of man. I have already

mentioned that Scheele states that he had obtained it by treating inspissated urine with nitric acid. According to Proust's statement if urine be evaporated to the consistence of syrup and treated with sulphuric acid, hippuric acid is precipitated amongst other substances in fine needle shaped crystals. By repeating this experiment I obtained needle-shaped crystals of sulphate of lime. Wurzer states the case of a man who after exposure to cold had at first a swelling of the paps and after the disappearance of this he passed a milky urine which contained only traces of the ordinary organic ingredients of the urine and no sulphates whatever, but on the other hand chlorohydric acid precipitated from the evaporated urine the above acid of which it cannot be decided, since hippuric acid was not then discovered, whether it was hippuric or benzoic acid though it was taken for the latter of them at the time. Its quantity amounted to one nine-hundredth of the original weight of the urine.

5. *Inorganic acids and bases.* Both sulphates and phosphates occur in human urine. The acids of these salts seem to be formed by the chemical operation of the kidneys, since only traces of sulphates and very small quantities of the phosphates are to be found in the other fluids of the body, while on the other hand the urine contains a large quantity of each. The sulphur contained in fibrin, albumen, &c., seems to be converted in the kidneys into sulphuric acid, while the other elements

combine to form ammonia, urea, &c. The same applies to phosphorus which is found in several of the solid tissues of the body. In the urine of herbivorous animals the phosphates are generally wanting while the carbonates are found in their place. Carbonic acid has also been sought for in human urine. Since it is acid it can only be contained as dissolved carbonic acid gas; but in diseases, and after the use of certain salts the urine may contain the carbonates of the alkalies. Proust concluded that it contained carbonic acid from the fact that urine yields a carbonated water by distillation; but this water contains carbonate of ammonia formed by the very process of distillation. Alexander Marcet, and afterwards Vogel placed a bottle containing urine and connected by a tube with one containing lime water, under the receiver of an air-pump. By exhausting the air carbonic acid was given off by the urine and rendered the lime water turbid. An experiment performed by myself did not afford the same results. The urine at first foamed, and particles of the foam passed through the tube into the lime water which thereby became turbid. But this did not take place after I had poured a stratum of olive oil as thick as my finger on the surface of the urine. Transferred whilst still warm to the receiver the urine yielded no gas bubbles through the oil until the pressure had been reduced to one inch of mercury. It then gradually yielded like common aerated water a small quantity of gas

until the pressure was reduced to one eighth of an inch, but this gas did not produce the slightest cloudiness in lime water. Wöhler repeated the same experiment after the free use of carbonated drinks without finding carbonic acid in the urine. These experiments prove that though carbonic acid may be found in the urine as dissolved carbonic acid gas it is by no means a constant but merely an accidental ingredient.

A very small quantity of silicic acid is also to be mentioned amongst the inorganic acids of the urine. It is separated by evaporating the urine to dryness and dissolving the residue in water, whereby a pulverulent mass remains from which the phosphate of lime is extracted by chlorohydric acid; the residue consisting of mucus, lithic acid, and silica, should be burned in the open air, when the silica will remain. All the water that we drink and with which our food is prepared contains dissolved silicic acid, which does not separate from it except by evaporation. This portion contained in the water passes with it through the liquids of the body and is separated with it by the kidneys.

The bases contained in the urine are, potassa, soda, ammonia, lime, and magnesia, a very small quantity of sesquioxide of iron, and sometimes a trace of the protoxide of manganese, all of which are divided amongst the acids according to their own as well as the acids' relative quantity and affinities, so that every acid takes hold of a certain

portion of every base, and *vice versâ* every base combines with a certain quantity of each acid, and it is only by evaporation and other analytical operations that certain salts separate in preference.

Chloride of potassium, sodium, and ammonium, and a small quantity of fluoride of calcium, appertain also to the salts of the urine; the latter exists generally in so inconsiderable a quantity that it can only be obtained by precipitating large quantities of urine with an ammoniacal solution of chloride of calcium and testing the washed and ignited precipitate for the presence of fluohydric acid in the usual way. The presence of this substance in the urine could be inferred *à priori* since it is contained in the bones and teeth. It must also be introduced in the body with the other earthy phosphates and again removed from it.

6. *Urea*. This is undoubtedly in every respect the most important ingredient of the urine; it imparts to it some of its peculiar characters. In regard to its composition and its crystallizable properties it stands on the borders between organic and inorganic substances. It combines with acids to form peculiar salts, in which respect it resembles the vegetable salt-bases. It is contained not only in the urine but, as we have already seen, in the blood also, when the secretion of urine is impeded, as for instance in cholera. It has even been found in the evacuations of the stomach during a retention of the urine. Several chemists, as Marchand and Barruel, have found it in the liquid, which collects

in different parts of the body in dropsy. It is also formed in several ways by the metamorphosis of other animal matters, both by processes within the living body and by chemical re-action without the body, of which I will state several instances. Urea is in urine combined with acids, in man with lactic acid, in cattle with hippuric acid, and in birds and reptiles with lithic acid. For this reason it cannot be obtained in crystals from concentrated urine, on account of which it remained undiscovered for a long time, and its combinations with acids have only recently been extracted from the urine by Cap and Henry.

Although it was first observed by Cruikshank, who discovered its property of crystallizing with nitric acid, yet it is to the excellent work of Fourcroy and Vauquelin on the urine that we owe our first certain knowledge of it. The name of urea was given to it by them. It was at first very difficult to obtain it in its pure state, and their first description of it shows that at that time they had not obtained it perfectly pure.

Urea may be obtained perfectly pure in the following manner. The urine should be evaporated in a water-bath as far as possible, and the residue extracted by anhydrous alcohol. The alcohol is then distilled in a water-bath, the yellow residue dissolved in a little water and digested with animal charcoal, which renders it almost colourless. The solution is then to be filtered and warmed to 122° F., and as much oxalic acid added as will dissolve

in it at this temperature. On cooling it deposits colourless crystals of oxalate of urea. If the temperature be raised to 212° F. when the oxalic acid is dissolved in it, the solution becomes dark brown and acquires a disagreeable smell. The oxalate of urea which then crystallizes has a beautiful red or sometimes brown colour. This colour can again be taken away by a little animal charcoal. When the acid mother-water is evaporated by a gentle heat it yields more crystals. Should it become charred and lose its strong acid taste, more oxalate of urea may be obtained by warming it and again adding oxalic acid. The crystals are collected and freed from the mother liquid by washing them with ice-cold water. They are then dissolved in warm water and a very small quantity of animal charcoal added and the solution filtered, which now yields snow-white crystals of oxalate of urea. The mother-liquid by evaporation yields a small portion of colourless crystals and crystallizes to the last drop. The crystals are dissolved in boiling water and mixed with extremely fine pulverized carbonate of lime which decomposes it with effervescence. When the solution ceases to redden litmus paper it is filtered from the deposited oxalate of lime and evaporated to dryness in a water-bath. A white saline mass is thus obtained, which consists of urea, but still impure from the presence of oxalate of potassa. This may derive either from a content of oxalate of potassa in the oxalic acid, which is sometimes the case, or from the urine when the

alcohol has not been perfectly anhydrous, and therefore dissolved chloride of potassium and sodium; finally the urea also contains some binoxalate of ammonia, which derives from the ammoniacal salts extracted by the alcohol. The urea is purified from all these substances by dissolving it in alcohol, the more anhydrous the better, which leaves undissolved a small quantity of a chemical combination of oxalate of potassa with urea.

There is still another method less circumstantial and which requires less expensive materials, but which does not with the same certainty give a pure urea. The urine is evaporated to the consistence of a thin syrup, the mass mixed with at least three times its volume of nitric acid of 1.22 to 1.3 specific gravity, which has been previously deprived by boiling of all nitrous acid. The mass is hereby converted into a thick paste of nitrate of urea which separates in a solid form. The vessel is then cooled in ice and transferred after four or five hours to a filter to drain. The filter is then placed on a dry brick and afterwards pressed between folds of bibulous paper. It is then dissolved in a very little boiling water and the combination once more crystallized, drained and pressed. The brownish salt now obtained is dissolved in warm water, digested with animal charcoal, and the uncoloured filtered solution saturated with carbonate of baryta or lead, and the solution evaporated in a water-bath to dryness. It generally resumes its yellow colour. The dry mass is then treated with

five times its weight of cold alcohol of 0.82 or stronger, which extracts the urea from the lead or barytic salt. The mixture should not be warmed lest a notable quantity of the salt be dissolved. The alcoholic solution is mixed with animal charcoal, four-fifths of the alcohol distilled off and the residue filtered while boiling hot. The urea crystallizes on cooling, and by farther evaporation still more is obtained, but the last portions are impure from an uncrystallizable combination of urea with the salt of lead or baryta, which combination is not insoluble in alcohol. The salt remaining after the treatment with alcohol likewise retains a portion of urea, which is lost unless it is again precipitated by nitric acid.

Cap and Henry prescribe that the inspissated urine be mixed while still warm with a sufficient quantity of lukewarm nitric acid, deprived of nitrous acid, without previous cooling of the syrup. A stronger reaction is hereby effected with strong effervescence which is principally caused by the decomposition of such matters as usually colour the nitrate brown, and on cooling the solution nitrate of urea is obtained in almost colourless crystals, which after draining, dissolving and crystallizing again are obtained quite pure. Cap and Henry state that little or no urea is lost by this treatment, but even should a little be lost it would be sufficient gain to dispense with the long method otherwise required for its discolouration. Cap and Henry dissolve the nitrate of urea in alcohol and

decompose it with carbonate of potassa. But in this way it is difficult to obtain it free from nitrate of potassa.

Urea has the following properties: by rapid cooling it crystallizes from its solution in fine needles of silky lustre, but by spontaneous evaporation in long thin four-sided prisms. In small quantities it only forms an efflorescence on the sides of the vessel. The best way of obtaining it in crystals is by slowly cooling a boiling saturated solution in alcohol. According to Prout it is always contaminated with a base when it crystallizes only in thin plates. It leaves a sensation of coldness on the tongue like that of nitrate of potassa, and is inodorous. It has neither acid nor alkaline reaction, and does not alter in the air except it be very moist and warm, when the urea deliquesces. According to Prout its specific gravity is 1.35. It fuses at 248° F. without decomposition, but at a few degrees above this it begins to boil; it then generates a large quantity of ammonia and sublimes some cyanate of ammonia without admixture of cyanide of ammonium. The fused mass becomes gradually pasty, and by cautious management of the heat a gray powder at last remains which is cyanuric acid, or the same acid which is formed by the dry distillation of lithic acid. By increased heat this is also decomposed with products peculiar to its decomposition. This behaviour was discovered by Wöhler. At 65° F. urea requires less than its weight of water

for solution; it is soluble in boiling water in all proportions. Its solution is accompanied by a great reduction of temperature. Its concentrated solution in water may be boiled without decomposition and preserved unaltered; but a dilute solution of it is decomposed both by boiling and by long keeping. The composition of urea is such that by decomposing one atom of water it forms one atom of carbonate of ammonia. This is the cause why urine both by ebullition and putrefaction yields so much carbonate of ammonia. Alcohol of 0.816 dissolves at 65° F. about one-eighth of its weight and about an equal weight of urea at the boiling point. On cooling, the urea deposits in very regular crystals. Ether and volatile oils dissolve only an inconsiderable trace of urea.

Urea like many other organic substances forms combinations both with acids and bases in fixed proportions, although it does not possess the power of neutralizing them.

Concentrated acids mixed with urea immediately produce its decomposition, the acid combining with ammonia, and carbonic acid passing off with effervescence. The same effect is produced by boiling urea with dilute acids. Nitrous acid seems to decompose it with especial facility.

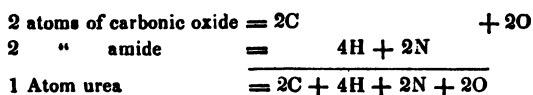
Urea has been analyzed with corresponding results by Prout, and by Liebig and Wöhler:—

| | Prout. | Liebig and Wöhler. | Atoms. | By Calculation. |
|------------|-----------------|--------------------|-------------|-----------------|
| Carbon . | 19.99 | 20.02 | 2 | 20.198 |
| Hydrogen . | 6.65 | 6.71 | 4 | 6.595 |
| Nitrogen . | 46.65 | 46.73 | 2 | 46.783 |
| Oxygen . | 26.63 | 26.54 | 2 | 26.425 |

Its atomic weight is 756.866; which is confirmed by the proportion in which it combines with nitric and oxalic acids.

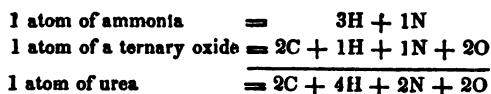
In regard to its theoretical composition it has been considered under different points of view. Wöhler showed that it had the same composition as the cyanate of the oxide of ammonium = $\text{NH}_4\text{O} + \text{C}'\text{NO}$, and that this latter salt may be dissolved in water without alteration, so that cyanate of lead and cyanate of silver may be precipitated by salts of lead and silver, but that by evaporation of the solution it is gradually wholly converted into urea which remains after the evaporation.

Dumas and other French chemists consider urea as an amide of carbonic oxide in which the carbonic oxide is combined with double the quantity of NH_3 , as in oxamide after the following diagram:



This view of its composition has, however, only in its favour the fact of its not being contradicted by the number of its elementary atoms, but the property of urea of combining with a base is evidently against it.

Urea, however, is hardly to be considered as the oxide of a compound radical since it contains two atoms of oxygen for every atom of acid with which it combines when it acts as a base, which does not agree with the behaviour of oxydized bases. Besides experiments by Regnault have proved that one atom of water enters into its combinations with oxacids, which cannot be separated from it without at the same time decomposing the urea, in which respect it resembles the vegetable salt bases, and which gives rise to the supposition that, as in the latter, the basic substance in urea is ammonia. The correctness of this view has yet to be proved by forming and analyzing combinations of urea with hydracids, whereby it might prove to be the case that, for instance, one atom of chlorohydric acid combines with one atom of urea without water. Regarded in this point of view urea will present the following composition :—



The metamorphosis of cyanate of the oxide of ammonium into urea, observed by Wöhler, would then merely consist in a metamorphosis of the cyanic acid into a substance of the same percentic composition as cyanuric acid, but only with two-thirds of its atomic weight. We know that cyanic

acid in its hydrous state passes at a few degrees above 32° F. into such a body, which is not cyanuric acid.

This view of the theoretical composition of urea, besides being more probable than that given by Dumas, coincides both with the formation of urea by evaporation of a solution of cyanate of ammonium, and with the behaviour of urea towards acids.

The combinations of urea with acids have been discovered by different chemists at different times. Cruikshank discovered the combination with nitric acid, Prout with oxalic acid, and Kodweiss that with cyanuric acid. He concluded from this that urea might be combined with most of the acids, but this was not practically accomplished until the investigations of Cap and Henry at the end of the year 1838, occasioned by finding a crystallized substance in the urine which was decomposed by hydrate of lime into urea and lactate of lime, induced them to endeavour to obtain combinations with some other acids; but as yet the number of known combinations with other acids is very limited. They may be produced in several ways. The easiest is by decomposing oxalate of urea with a salt of lime containing the acid with which urea is to be combined. Perhaps also it might be accomplished by mixing nitrate of urea and the salts of baryta, or oxide of lead, or an alkali with the acid in atomic proportions, and evaporating the solution in a water-bath to dryness, and extracting the salt of urea thereby formed, by anhy-

drous alcohol. Cap and Henry also mix the acid with pure urea in atomic proportions and evaporate.

Sulphate of urea is obtained when the oxalate of urea is dissolved in twice its weight of water, the solution precipitated by newly precipitated and washed sulphate of lime, till all the oxalic acid is combined with the lime, then decanting the solution, precipitating the dissolved sulphate of lime by alcohol, and evaporating the filtered solution, which yields sulphate of urea in granular or needle-shaped crystals.

Nitrate of urea crystallizes from its solution on cooling in large shining plates. By spontaneous evaporation it effloresces more than any other salt on the sides of the vessel; but at the same time firm, transparent, prismatic crystals are formed in the liquid. It has a pure acid taste, is easily soluble in water and alcohol, and remains unchanged in the open air. According to Prout it at first yields by dry distillation a combustible gas and is converted into nitrate of ammonia, which is afterwards decomposed in the usual manner without any residue of carbon. It swells up when heated quickly on a platinum dish. A considerable reduction of temperature is produced by its solution in water. From the saturated solution the greater part is precipitated in small scales by the addition of a sufficient quantity of nitric acid. Oxalic acid precipitates oxalate of urea. By boiling its watery solution carbonic acid is generated with effer-

vescence and the salt converted into nitrate and carbonate of ammonia. According to Prout's analysis nitrate of urea consists of 47·37 nitric acid and 52·63 urea. Regnault has analyzed this salt by combustion with oxide of copper and obtained the following results:—

| By Experiments. | Atoms. | By Calculation. |
|--------------------------|-------------|-----------------|
| Carbon . 10·04 | 2 | 9·886 |
| Hydrogen 4·09 | 5 | 4·035 |
| Nitrogen 34·29 | 3 | 34·344 |
| Oxygen . 51·58 | 8 | 51·735 |

Which proves that it consists of one atom of urea, one atom of nitric acid, and one atom of water. Without this content of water the salt ought to have yielded 10·67 per cent. of carbon, 3·48 of hydrogen, and 37·03 of nitrogen.

Oxalate of urea crystallizes in thin, long, laminated crystals, which become broader, the slower it crystallizes. It has a pure acid taste. By heat it fuses and boils, whereby carbonate of ammonia is generated and cyanuric acid formed exactly as from urea alone. The oxalic acid is thereby converted into carbonic acid and carbonic oxide. If the salt contain oxalate of potassa a little cyanide of ammonium is formed, and a carbonaceous residue remains which contains the alkali. It dissolves in large quantity in boiling water and crystallizes by cooling. At 60° F. one hundred parts of the solution contain only 4·16 parts of the salt, or one hundred parts of water dissolve 4·37 parts of the salt. A portion of it is again precipitated

by an excess of oxalic acid. It dissolves with more difficulty in alcohol than in water, and the difference between its solubility in boiling and cold alcohol is much less than with water. One hundred parts of alcohol of 0·833 dissolve at 60° F. only 1·6 parts of oxalate of urea. According to my analysis it consists of 37·436 oxalic acid and 62·564 urea, the oxygen of which is in proportion to that of the acid as 2:3. But Regnault has shown that the salt even after drying at the highest temperature it can bear without decomposition, that is at 230° F., contains one atom of water, which is proved by the elementary analysis. It yields no more than 23·11 per cent. of carbon, when without the content of water it ought to have yielded 25·26 per cent. On the other hand it yields 4·79 per cent. of hydrogen, which corresponds exactly with its containing one atom of water, without which the hydrogen would only have amounted to 4·13 per cent. Oxalate of urea seems to combine with neutral oxalate of potassa to a double salt, which is soluble in alcohol, and which is decomposed by lime, so that oxalate of lime precipitates, and urea remains in the solution with the oxalate of potassa. This combination is neither dissolved nor decomposed by alcohol,—and when dissolved in water and evaporated it yields a thick syrup, which gradually hardens to a colourless saline mass.

Cyanurate of urea is obtained by boiling the acid with a concentrated solution of urea; it

should be filtered while hot and allowed to cool, when the salt will crystallize in prisms. It is also obtained as already observed above by the dry distillation of urea. It is soluble in alcohol. It is decomposed by nitric acid forming nitrate of urea and separating cyanuric acid. It is best to employ a very dilute solution.

Lactate of urea is obtained, according to Cap and Henry, by evaporating the urine in a water-bath to a syrupy consistence, and treating the residue with alcohol. This dissolves the lactate of urea, free lactic acid, and other matters soluble in alcohol. The alcoholic solution is then distilled until there is but a small residue, the free acid of which is saturated by oxide of zinc. The solution is then filtered, evaporated in a water-bath to dryness, the residue treated with anhydrous alcohol, and left to spontaneous evaporation, whereby the lactate of urea crystallizes. It is obtained artificially by precipitating a solution of oxalate of urea exactly by a solution of lactate of lime. The filtered solution is evaporated in vacuo over sulphuric acid, which causes the crystallization of the salt in long, colourless six-sided prisms. It gives a sensation of coldness to the tongue like that occasioned by nitrate of potassa, it absorbs moisture from the air and deliquesces. It is easily soluble in water and alcohol, but sparingly so in ether. It fuses by heat. Cap and Henry also mention that it chars by a strong and rapid heat, and is decomposed; but that by a certain tempe-

rature it may be sublimed unaltered. This statement seems to prove that the lactate of urea yields a crystalline sublimate, but Cap and Henry do not mention any experiments to prove the unaltered nature of the salt. It is scarcely probable that it should be unaltered since neither the acid, nor the urea, nor even the lactate of ammonia is volatile. Their supposition of the volatility of the lactate of urea carries them even so far as to contend that more than half of it is volatilized during the evaporation of the urine. This they suppose on the ground that they were not able to separate more than about one-third of the urea in the urine as lactate of urea. But this evidently arises from imperfection in the experiment, for if such volatilization took place it would not have been possible to find the content of urea from which they calculated the loss, since every analysis of the urine must be commenced by evaporation.

Lithate of urea exists, according to the same chemists, in the excrements of birds and reptiles which are known to evacuate the urine with the excrements. By treatment with hydrate of baryta the urea separates, and may be extracted from the residue after evaporation in a water-bath, by anhydrous alcohol. The combination of lithic acid with urea has not been described, nor its properties made known.

Hippurate of urea was obtained by them from the urine of horses and cattle by inspissation and extraction by alcohol. The alcoholic solution was

evaporated by a gentle heat to the consistence of paste, well pressed, and the solid part dissolved in boiling anhydrous alcohol. This solution yielded by evaporation fine needle-shaped crystals of hippurate of urea. It is most easily obtained by double decomposition of the oxalate of urea and hippurate of lime.

Urea also combines with bases. The stronger bases decompose it when heated, and combine with carbonic acid during the generation of ammonia. But the weaker bases, especially such metallic oxides as combine in preference with animal matters, form with it insoluble compounds. They are best obtained by mixing a solution of metallic salt with a solution of urea in excess, and afterwards adding the alkali to saturate the acid of the metallic salt. The oxide then precipitates in combination with the urea. Prout, who discovered this circumstance, states that the combination of oxide of silver with urea is gray, and deflagrates by heat, leaving metallic silver. It also combines with oxide of lead, even by digestion of a concentrated solution with the oxide. The combination is easiest obtained when nitrate of urea is decomposed by carbonate of lead in excess. The mass is evaporated to dryness, and treated with alcohol, which dissolves the combination and deposits it after evaporation as a tenacious syrup. It deliquesces in moist air and becomes more liquid. It is easily dissolved by water. Urea is considered to be the cause of the

crystallization of chloride of sodium and ammonium in the less usual form of octohedrons. It is said to produce the alteration with chloride of sodium, even when present in so small quantity as to be separated with difficulty, wherefore it has been proposed as a test for the presence of urea to dissolve a little chloride of sodium in the solution and leave it to spontaneous evaporation. The form of the chloride of sodium will then indicate the presence of urea. This test may, however, be considered rather uncertain. Urea combines with many salts whose solubility and form of crystallization is thereby altered, without the possibility of extracting it by alcohol from these combinations. No salt of the metals is precipitated by a solution of urea, neither is an infusion of galls.

The formation of urea in the body seems to be produced by the vital processes which gradually metamorphose a part of the living solid tissues and convert them into urea. It is not a product of excessive or indigestible food, and its secretion with the urine continues uninterruptedly in diseases when no food is taken, during long continued fasting, and even when animals are fed on substances which contain no nitrogen, for instance, on starch or sugar, though they at last emaciate and die from weakness. Marchand performed some experiments on a lean dog which he fed at first freely with milk. At the expiration of five days the urine contained 2.6 per cent. of urea,

which in the following five days increased to 3 per cent. Its diet was now changed to water and ten ounces of sugar candy per diem. The dog at first was perfectly satiated with this. At the end of six days the content of urea in its urine decreased only to 2·8 per cent.; in the following five days to 2·4 per cent.; and in the following five days to 1·8 per cent. After the expiration of twenty days the dog was extremely emaciated and feeble. The diet was now changed to soup and milk, whereby its strength and flesh were soon restored, and after fourteen days the urine contained 3·5 per cent. of urea.

Urea has been used and recommended by some French physicians as a diuretic; but its action should be farther ascertained before it is relied on for this purpose.

7. *Undetermined animal matters of the urine.* Besides the foregoing the urine contains several, perhaps many organic matters in mixed solution. They form the yet uncertain part of our knowledge of the urine, and it is very difficult, not to say impossible, to give an exact account of them. One does not know what to look for. There is no known test which has a peculiar and characteristic reaction with each ingredient. The examinations must therefore be made at random, and it is impossible to say that the substance found and considered peculiar is not composed of several. In the mean time I will here give the examinations which I have made and their results.

The odorous matter of the urine is first to be considered. Warm urine exhales an aromatic odour by no means unpleasant, which increases, though it is altered slightly, by evaporation; and when the urine has been concentrated to the consistence of a syrup, and kept for some time at a temperature between 160° F. and 176° F. for farther concentration, it assumes the same odour as a solution of reduced indigo at the moment it is precipitated by an acid. It is very probable that a part of this odour derives from the evaporation of a volatile odorous matter, but the odour towards the end of the operation is probably, like that of musk and castor, a consequence of the generation of ammonia which carries with it small particles of substances otherwise not volatile.

If urine be concentrated to the consistence of a thick syrup, and mixed in a well corked bottle with ether, and the mixture heated to 97° F., which renders the syrup so liquid that it may be shaken up with the ether, the latter is thereby rendered distinctly yellow. The mass should then be permitted to cool, the ether decanted from the congealed syrup, and the treatment with ether repeated as long as it extracts any thing, when the collected ether should be mixed with some water and distilled. If the distillation be interrupted before all the ether has been distilled, the ether will be found to be much more coloured than the subnatant water. The two solutions are to be separated and each evaporated alone. The water

leaves an extractive matter which tastes bitter, reddens litmus paper, and generates ammonia with lime and hydrated oxide of lead. By the latter a soluble salt of lead is formed, from which after decomposition by sulphuretted hydrogen and subsequent evaporation, a yellow extractive bitter mass is obtained, in which crystals are formed. It seems to be a mixture of free lactic acid, lactate of lime, and lactate of ammonia, perhaps also urea and one of the extractive matters of the urine. Their quantity is very small. The crystals are too soluble in water to be hippuric acid.

On evaporation of the ethereal solution, a yellow, transparent, viscid mass remains with a peppery and pleasant odour, a sharp and aromatic taste, which like fat is not moistened by water, though by heating the water it becomes white and dissolves into a pale yellow liquid, leaving a very small quantity of a brown fatty oil undissolved, which strongly reddens moistened litmus paper. The watery solution has an empyreumatic taste, reddens litmus paper, exhales by evaporation an aromatic, rather peppery odour, and at last leaves the same yellow viscid transparent water which it dissolved. Alcohol dissolves it easily. The hydrated oxide of lead decomposes it into two matters, of which the one combines with the oxide of lead to a soft, pasty mass, but the other dissolves in water although with difficulty, and after decomposition by sulphuretted hydrogen and evaporation

poration it yields a transparent yellow matter, which reddens litmus paper, has a bitter, afterwards sweet taste, and shows no trace of crystallization. The pasty mass after decomposition by chloro-hydric acid, gentle drying and extraction by alcohol, leaves a reddish brown matter with a sharp pungent taste, which reddens litmus paper strongly, feels viscid like fat, is not moistened by water but after a while dissolves in it sparingly, leaving a red fat oil. Water dissolves the above-mentioned substance and by heating the solution it smells like fresh urine. These matters are not identical with any others in the body, and I do not know whether they occur in every urine.

If the residue from the treatment of inspissated urine with ether be extracted by alcohol of 0·833 as long as any thing is dissolved, the alcohol distilled off, the residue dried in a water-bath as much as possible, and afterwards treated with anhydrous alcohol the greater part of it is dissolved. Urea crystallizes after distillation of the anhydrous alcohol, and when no more will crystallize the thick mass should be laid on folds of bibulous paper and pressed gently at first, but afterwards more strongly, till the paper has absorbed the uncrystallized portion. After removal of the urea, the paper should be well extracted with water, and the filtered solution evaporated in a water-bath. A thick yellow syrup is hereby obtained in which only traces of crystals are observed, and which consists of a yellow extractive matter impure from

the presence of urea, lactates and sal-ammoniac. The yellow colour is not characteristic of it, for when treated with animal charcoal, and heated, it becomes colourless, yielding by evaporation a colourless extract of the same properties. It easily becomes yellow by heat. This matter is also obtained after the precipitation of the urea by oxalic acid, by precipitating the excess of the latter by lime, filtering the solution, and evaporating it in a water-bath. It is then free from oxalic acid, but contains a soluble salt of lime. Where concentrated it remains soft while warm, but becomes tough on cooling without hardening, its taste is bitter and at the same time saltish from an admixture of lactate of ammonia and sal-ammoniac, it is inodorous until it is dissolved in sufficient water to form a dilute syrup, when it exhales an offensive urinous odour. I thought that this odour, derived from an admixture of urea and a slight generation of ammonia from it, because the odour is immediately exhaled, when ammonia is added. It becomes moist in the air, and is very soluble in alcohol. Heated to decomposition, it at first exhales a urinous smell, afterwards one of broiled herring, it then puffs up, chars, smells like burnt horn, and yields by dry distillation oil of Dippel, water, sal-ammoniac, and carbonate of ammonia, and leaves a porous, rather incombustible carbon, which, however, leaves but a slight trace of ashes. The watery solution of this matter has the following reactions. It is not precipitated, or but slightly

so, by bichloride of mercury in excess, and not more so by neutral acetate of lead or an infusion of galls. A slight turbidness sometimes occurs from the presence of other matters. On the other hand, the solution is precipitated by subacetate of lead, protochloride of tin, and nitrate of silver; all of these precipitates contain animal matter in combination with the precipitated salt. The precipitate by oxide of lead is a combination of basic chloride of lead with basic lactate of lead. The precipitate by tin, is basic lactate of tin, and that by silver is chloride of silver, all combined with animal matter. The latter is decomposed by heat, yielding the smell of burnt horn, and leaving a carbonaceous mass. By decomposition of the precipitate by the oxide of lead, by sulphuretted hydrogen a yellow acid solution is obtained which contains lactic and chlorohydric acids. If these be saturated with carbonate of barytes and the solution evaporated, an extractive mass is again obtained like the original solution, which was decomposed. In like manner very little of it is dissolved by anhydrous alcohol, because the extractive matter is merely freed from urea and transferred to other salts insoluble in alcohol. Heated to the decomposition of the animal matters, it leaves a mixture of carbon, chloride of barium, and carbonate of baryta. Dissolved in water, and mixed with a solution of carbonate of ammonia, but in insufficient quantity to decompose all the barytic salt, a brownish-yellow carbo-

nate of baryta is precipitated which, when collected on a filter, washed with cold water and afterwards digested with caustic ammonia, yields the animal matter to ammonia and is left after evaporation as a yellow extract without urinous odour, but which in other respects resembles the extract from flesh, soluble in anhydrous alcohol. A solution exactly resembling this, is obtained when the animal charcoal employed for the discolouration of the extractive matter in question is digested with dilute caustic ammonia and the filtered solution evaporated. If carbonate of ammonia be added to the combination of the extract with chloride of barium, in such excess as to decompose all the chloride of barium and also be present in excess, the animal matter combines with the sal-ammoniac and a mass mixed with crystals is obtained, which is likewise insoluble in anhydrous alcohol, and which, when moistened with a little caustic ammonia has an odour of spoiled urine.

In order to ascertain whether the solution retains any thing after precipitation by acetate of lead, it was precipitated by sulphuretted hydrogen and evaporated, whereby an extractive matter was obtained having the smell of acetic acid, but by the addition of chloride of barium and evaporation, I obtained exactly the same combination as that precipitated by the subacetate of lead, so that the precipitate was only caused by the presence of chloride of ammonium and lactate of ammonia in the solution. I afterwards found that

when urea is mixed with the extract which combines with the chloride of barium, the urea is also taken up by the salts, and I endeavoured in vain to combine the extract in this manner, and to dissolve the urea alone in alcohol. The conclusion of all these experiments is that the portion of inspissated urine, which dissolves in anhydrous alcohol, contains besides urea, lactic acid, lactate of ammonia and chloride of ammonium, an extractive matter which, after complete isolation, has great similarity to the corresponding extractive matter from a solution of flesh, and the decomposition of which when in combination with urea produces the offensive urinous odour which is observed during putrefaction of urine. One of the distinguishing characteristics of this matter is, that it combines with great eagerness with salts, and thereby alters their solubility in alcohol, according to the different nature of these salts. As it is a great convenience to have separate names for peculiar matters I might name this matter *halophile*, but in consideration of the evil which arises from the introduction of peculiar names for substances which perhaps are only mixtures, of which the manifold use of the name *osmazome* affords an instance, I have preferred to call this substance *extractive matter of the urine soluble in anhydrous alcohol*.

What anhydrous alcohol leaves undissolved from the substances extracted from inspissated urine by alcohol of 0.833, is also an extractive matter. If

it again be treated with a small quantity of alcohol of 0·833 an animal matter is dissolved, leaving chloride of sodium, not containing a great deal of the former. If this solution in alcohol be evaporated by itself, a clear, transparent, yellowish extract is obtained, free from all crystalline admixtures. It behaves as follows: it tastes exactly like the corresponding extract from flesh, does not at all smell urinous, reddens litmus paper, puffs up when heated, like tartrate of potassa, and leaves a porous alkaline coal. It therefore contains lactate of potassa. By dry distillation it yields ammoniacal water, and an empyreumatic oil. Its watery solution is not precipitated by bichloride of mercury, by neutral or basic acetate of lead, nor even by tannic acid. When an inconsiderable precipitate appears as is sometimes the case, the alcohol employed has been weaker than 0·833 so as to have taken up some of the substances soluble only in water. It is not made turbid by acids nor alkalies, nor by passing chlorine gas through it. I will name it *extract of the urine, soluble in alcohol of 0·833*. It is possible that it may be the same as the previous extractive matter, but merely rendered insoluble in anhydrous alcohol by its combination with the alkaline lactates.

We have seen that alcohol of 0·833 leaves a portion of the inspissated urine undissolved, which likewise is an extract, reddens litmus paper, and contains an admixture of a great portion of the sulphates and phosphates. It derives its acid re-

action from lactic acid. If this latter be saturated with carbonate of ammonia and evaporated, alcohol of 0.833 will dissolve a little lactate of ammonia mixed with extractive matter. If the free acid be saturated with ammonia at the beginning of the examination, all lactic acid will be extracted by alcohol from the residue. In order to extract the animal matter from the residue, insoluble in alcohol, the following method is to be pursued. It is dissolved in water, which leaves phosphate of lime, lithic acid, silica and mucus undissolved. The solution is then precipitated by acetate of baryta as long as any precipitate forms. This is sulphate of baryta, but combined with an animal matter, which chars and smells ammoniacal by ignition after it has been washed and dried. I do not know the nature of this substance. After the precipitation of all the sulphuric acid the solution is made alkaline by caustic ammonia, and precipitated by acetate of baryta; this precipitate is basic phosphate of baryta, likewise in combination with a large quantity of animal matter. In my attempt to isolate the latter it always followed the phosphoric acid, so that it could be transferred from one phosphate to another, but not from a phosphate to any other salt. I do not know the nature of this substance either; perhaps it is analogous to that which I shall mention when on flesh. By ignition the phosphate of baryta smells like burnt horn and chars. The alkaline solution is evaporated to expel the excess of ammonia, or still better,

is saturated as exactly as possible with acetic acid. It is then precipitated by a solution of neutral acetate of lead, which does not, however, produce a copious precipitate. After washing, decomposition by sulphuretted hydrogen, and evaporation of the solution, a grayish brown, transparent, extractive matter is obtained, which keeps dry in the air, has no taste, scarcely reddens moistened litmus paper, and the watery solution of which is but sparingly precipitated by bichloride of mercury, rather more copiously by chloride of tin, and is completely precipitated by acetate of lead. An infusion of galls produces a dark gray coloured precipitate.

The solution with neutral acetate of lead is strongly precipitated by the addition of basic acetate of lead. When the white precipitate is collected together it becomes yellowish. It generally contains an admixture of a portion of basic chloride of lead derived from the chloride of sodium, which the alcohol has not effectually separated from the inspissated urine. By decomposing the well washed precipitate by sulphuretted hydrogen, a yellow acid solution is obtained containing chlorhydric acid. The acid is saturated with carbonate of ammonia, the solution evaporated almost to dryness, after which it is mixed with alcohol of 0.833, which dissolves the sal-ammoniac and leaves an animal matter, which should be well washed with alcohol and dried. It has a yellow brown colour, is opaque in mass, has a feeble bit-

ter taste, keeps dry in the air, and dissolves in water with a dark yellow colour. It is not precipitated by bichloride of mercury, but perfectly so, and with a dark brown colour, by protochloride of tin, basic acetate of lead, and nitrate of silver. It is only slightly precipitated by an infusion of galls, even after the lapse of several hours.

After the above solution from the residue of the urine, insoluble in alcohol, has been precipitated by basic acetate of lead, it still contains animal matters. If the oxide of lead be precipitated by sulphuretted hydrogen a colourless solution is obtained, which becomes yellow after evaporation in a water-bath. After it has become perfectly dry it is treated with very little anhydrous alcohol, which dissolves it all; the solution is then diluted with more alcohol as long as any precipitate is formed. White flocculi hereby separate, which, when transferred to a filter and washed with alcohol, form, when dry, a shining, transparent, yellowish brown mass. Dissolved in water, filtered, and evaporated, it leaves a pale yellow, cracked, transparent mass, resembling gum arabic. It has no taste, puffs up by heat, smells like burnt horn, and leaves a very porous coal, which yields phosphate of lime when reduced to ashes. It is soluble in water with a pale yellow or no colour; and the solution is precipitated by bichloride of mercury, protochloride of tin, and nitrate of silver. The last-mentioned precipitate has a dirty orange colour. An infusion of galls pro-

duces merely a slight precipitate, probably only in consequence of an admixture of other substances.

The solution from which the foregoing substances have been precipitated by anhydrous alcohol, still contains an animal matter which colours the spirituous solution yellow.

Albumen is sometimes enumerated amongst the ingredients of the urine. It is in fact very often found in urine, but it must always be considered as the consequence of a sickly or, at least, a feeble state of health. It is recognised when the urine yields a strong precipitate with infusion of galls, nitric acid, and bichloride of mercury, and by becoming more or less turbid by heat. By dissolving the residue from the evaporation of healthy urine, in water, a portion remains undissolved, which can for the greater part be dissolved by concentrated acetic acid. This solution is precipitated by ferro-prussiate of potassa, but in its outer appearances it does not resemble a solution of albumen in acetic acid; it is a solution of the mucus of the bladder, and is precipitated in combination with cyanide of iron.

It is stated by Nauche, that another substance always occurs in the urine of pregnant women. It has been called *Kyestein* (from *xviii*, to be pregnant, and *stein*, pellicle) because it forms a covering about a line in thickness on the surface of the urine of pregnant women, which has been allowed

to stand for a few days. This consists of a tissue of flocculi and long filaments. A portion of it subsides and forms a white layer at the bottom of the vessel. The pellicle at the surface is coherent, and adheres closely to the sides of the vessel. The chemical nature of this substance has not yet been examined. Rousseau found it in the urine of pregnant monkeys. Nauche states, that the occurrence of Kyestein in the urine affords a true means of ascertaining the state of pregnancy, especially when it is two or three months advanced.*

After this general enumeration of the ordinary ingredients of the urine, I will give the results of an analysis of it performed by me in the year 1809. But at that time several facts mentioned in a former part of this treatise in regard to the

* The July Number of the *American Journal of the Medical Sciences* for 1842, contains an *Essay* by Dr. Elisha K. Kane, in which he determines the value of Kyestein as a proof of pregnancy. Dr. Kane examined the urine of nearly one hundred pregnant and nursing women, and arrived at the following general conclusions:—

1. "That the Kiesteine is not peculiar to pregnancy, but may occur whenever the lacteal elements are secreted without a free discharge at the mammæ.
2. That though sometimes obscurely developed, and occasionally simulated by other pellicles, it is generally distinguishable from all others.
3. That where pregnancy is possible, the exhibition of a clearly defined Kiesteinic pellicle, is one of the least equivocal proofs of that condition; and,
4. That when this pellicle is not found in the more advanced stages of supposed pregnancy, the probabilities, if the female be otherwise healthy, are as 20 to 1 (81 to 4) that the prognosis is incorrect."—*Translators.*

organic ingredients of the urine were unknown. The analysis gave the following results:—

| | |
|--|---------|
| Water | 933.00 |
| Urea | 30.10 |
| Free lactic acid | } 17.14 |
| Lactate of ammonia | |
| Extract (of flesh) soluble in alcohol | |
| Extractive matter soluble only in water | |
| Lithic acid | 1.00 |
| Mucus of the bladder | 0.32 |
| Sulphate of potassa | 3.71 |
| Sulphate of soda | 3.16 |
| Phosphate of soda | 2.94 |
| Biphosphate of ammonia | 1.65 |
| Chloride of sodium | 4.45 |
| Chloride of ammonium | 1.50 |
| Phosphate of lime and magnesia | 1.00 |
| Silica | 0.03 |
| | 1000.00 |

Urine of Animals.—As yet the urine of but very few animals has been examined. Urea has generally been found occur in the urine of the higher classes of animals. The urine of carnivorous animals is acid, but soon becomes alkaline from the formation of ammonia, which is partly the cause of its peculiarly offensive odour. Vauquelin who was the first to examine the urine of lions and tigers found it alkaline, but Hieronymus has shown that when fresh it reddens litmus paper. Vauquelin found it to contain much urea, and that this could be easily obtained colourless. But on the other hand he found no lithic acid. Hieronymus confirmed the former, but found

lithic acid in determinable quantity. It is, therefore, erroneous to suppose, that this acid occurs amongst mammalia only in human urine, and the statement of Coindet that it is wanting in the urine of monkeys is still doubtful. On the other hand lithic acid occurs in the urine of birds, amphibia, and fish; and Jacobsen has shown that it is also formed in the kidneys of the mollusca. Earthy phosphates are only found in acid urine, and alkaline phosphates in that of carnivorous animals, but are wanting in that of herbivorous animals.

Urine of lions, tigers, and leopards has been examined in its fresh state by Hieronymus, and seems to be all alike. It is clear, light yellow, with a strong, unpleasant odour, and an acid, nauseous and bitter taste. At a temperature of 50° F. to 55° F. the specific gravity of urine from the same animal varies between 1·059 and 1·076. Soon after evacuation it becomes alkaline from the formation of carbonate of ammonia. This may, however, be expelled by heat when the urine becomes acid again. White coagulated flocculi separate by evaporation, and after sufficient concentration the greater part of the urea is deposited in crystals. The analysis of the urine of these three animals gave:—

| | |
|--|---------|
| Urea, animal matter soluble in alcohol (osmazome) and free lactic acid | 13.220 |
| Lithic acid | 0.022 |
| Mucus | 0.510 |
| Sulphate of potassa | 0.122 |
| Sal-ammoniac with some chloride of sodium | 0.116 |
| Phosphates of lime and magnesia with a little carbonate of lime | 0.176 |
| Phosphates of potassa and soda | 0.802 |
| Phosphate of ammonia | 0.102 |
| Lactate of potassa | 0.330 |
| Water | 84.600 |
| | <hr/> |
| | 100.000 |

I have here altered acetic into lactic acid for reasons already made known. An attentive reader may also, perhaps, be struck by the enumeration of carbonate of lime amongst the ingredients of an acid solution. This incorrectness arises from the circumstance that the amount of some of the ingredients has been ascertained by incineration, which decomposes the lactate of lime and converts it into a carbonate. Hieronymus found the same ingredients in the urine of the hyena and panther. The urine of the former had a specific gravity of 1.061 at 50° F., and the latter 1.045 at a temperature of 48° F.

The urine of the *rhinoceros* has been examined by Vogel. It is turbid and yellow, and looks like clay-water mixed with ochre. It has a peculiar odour, not unlike that of mashed ants; in the air it becomes darker from the surface downwards, and is covered by a pellicle of small crystals of

carbonate of lime. It effervesces with acids and becomes clear. If allowed to clarify spontaneously, it deposits a yellow powder which amounts to $2\frac{3}{4}$ per cent. of the urine, and consists of the carbonates of lime and magnesia combined with an azotic animal matter, and mixed with sesquioxide of iron and silica. The clarified urine is dark yellow, and forms by evaporation a new deposit of carbonate of lime and magnesia, which were dissolved in the urine as bicarbonates. If the urine be evaporated to one-third of its volume, filtered and mixed when cool with chloro-hydric acid, a precipitate of hippuric acid is formed which consists of 0.45 per cent. of the urine, and which was combined in the urine with potassa. Urea and the ordinary salts are also contained in it.

The urine of *elephants* has also been examined by Vogel. It is turbid from carbonate of lime and magnesia floating though it, and it clarifies with difficulty. It contains no trace of hippurate of potassa, but on the other hand urea is more abundant than in that of the rhinoceros. It does not contain the brown oil which, according to Fourcroy and Vauquelin, may be obtained from the urine of cows and horses. Brandes, who afterwards examined the urine of elephants, found hippuric acid in it combined both with an alkali and urea. After inspissation of the urine, ether extracted a small quantity of a pasty fat, and alcohol extracted an animal matter which was precipitated by an infusion of galls.

The urine of *horses* was examined by Fourcroy and Vauquelin, and by Chevreul. It is yellow, not unfrequently turbid, has a peculiar unpleasant odour, and a saline, bitter, afterwards sweetish taste. It deposites on standing a mixture of carbonate of lime and magnesia, which blacken by ignition. Its specific gravity is between 1·030 and 1·050. It has an alkaline reaction, and effervesces with acids. It becomes darker by exposure to the air, and by evaporation deposites still more of the carbonates combined with an animal matter. After evaporation it leaves about 0·05 residue, four-fifths of which is dissolved by alcohol. The insoluble part consists principally of carbonate of soda. Chloride of sodium first crystallizes from the alcoholic solution, and afterwards hippurate of soda in brown lamina. If the alcohol be evaporated and the residue dissolved in a little water, chlorohydric acid will precipitate hippuric acid from it. When urea was precipitated by nitric acid from the concentrated urine, and the acid solution pressed out and saturated with alkali, Fourcroy and Vauquelin obtained a small mass of reddish solid fat, with a sharp taste, which volatilized easily with the vapours of water, dissolved easily in alcohol, and combined with acids. They also state that this fat was obtained by distillation from the urine of herbivorous animals, and that it is the cause of its odour and colour. They found in the urine of horses: urea 0·7, hippurate of soda 2·4, carbonate of soda 0·9, chloride of potassa 0·9, carbonate of lime, from 0·2 to 1·1, water,

(with some mucus and strong fat) 94.0. Chevreul also found sulphate of lime dissolved in the urine of horses.

The urine of camels has been examined by Chevreul. It yielded, by distillation, carbonate of ammonia and a volatile oil, on which its odour depends. By the addition of nitric, sulphuric, and chlorohydric acids, it acquires a pink colour; this property is peculiar to the volatile oil. It deposits by boiling a mixture of carbonate of lime and magnesia in combination with animal matter and silica. From the inspissated urine nitric acid precipitates a large quantity of nitrate of urea. Besides these it contains chloride of sodium, hippurate of soda, carbonate of soda, sulphate of potassa in larger quantity, some sulphate of soda and carbonate of ammonia, and a trace of the sesquioxide of iron. Phosphates and lithates are altogether absent.

The urine of *horned cattle* has not been examined since the time of Rouelle. It is known to contain urea in larger quantity than the urine of men, and also hippurate of soda. Exposed to the air, it deposits small crystals of carbonate of lime and magnesia.

The urine of *swine* has been examined by Lassaigne. It is pale yellow, clear and transparent. It contains urea, sulphates of potassa and soda, chlorides of potassium, sodium, and ammonium, and traces of carbonate and sulphate of lime.

The urine of *beavers* contains, according to the

examination by Vauquelin, dissolved carbonate of lime and magnesia, which precipitate by evaporation, urea, hippurate of soda and the other ordinary ingredients of the urine of herbivorous animals, but no phosphates nor lithic acid. It also contains an unaltered vegetable substance derived from willow-bark, which is the principal food of this animal, and which may be detected by placing a piece of cloth soaked in alum in the urine of the beaver, when it will become coloured exactly as if it had been placed in an infusion of willow bark.

The urine of *rabbits* and *guinea pigs* was also examined by Vauquelin; it has an alkaline reaction, effervesces with acids, precipitates carbonate of lime by exposure to the air, and contains, besides urea, the ordinary salts of the urine of herbivorous animals.

The urine of *birds* is peculiar from its large content of lithic acid, existing ordinarily as bilithate of ammonia. The urine of carnivorous birds contains urea, according to Coindet, though this substance is wanting in that of granivorous birds, which contains lithate of ammonia. The urine of vultures also contains a green colouring matter. Fourcroy and Vauquelin found in the urine of the ostrich: lithic acid to the amount of $\frac{1}{10}$ of its weight, an animal matter, sulphate of potassa, sulphate of lime, sal-ammoniac, an oleaginous substance and acetic acid, though the existence of this last is doubtful.

The urine of *serpents* is a small coloured liquid,

which, soon after evacuation, hardens to a white, earthy mass, consisting of lithic acid, bilitates of potassa, soda, and ammonia, and some phosphate of lime. When boiled with alcohol a small yellowish extractive mass is obtained which contains no crystals of urea. I again refer to the statement of Cap and Henry, that urea may be obtained from it by saturating the lithic acid with hydrate of baryta.

The urine of *frogs* is altogether of a different nature. According to J. Davy, that of the *Rana taurina* is a liquid of 1.003 specific quantity, containing chloride of sodium, urea, and a little phosphate of lime dissolved. That of the *Bufo fuscus* has a specific gravity of 1.008, contains more urea, chloride of sodium, and phosphate of lime, than the former. Magnus found in the urine of the *Testudo nigra*, a great deal of lithic acid, no hippuric acid, and very little but a determinable quantity of urea.

b. ACCIDENTAL INGREDIENTS OF THE URINE.

The urine sometimes contains ingredients which are accidentally present, and derive either from the use of uncommon substances as food, or are the consequences of disease by which the nature of the urine is altered.

Accidental ingredients from foreign matters introduced into the body.—Substances introduced by

the mouth or absorbed by the skin without being afterwards altered by the vital processes, are evacuated with the urine soon after they have been dissolved in the liquids of the body. In this manner certain ingredients of the food impart peculiar substances to the urine, as for instance asparagus, which communicates a very disagreeable smell to the urine of those who use it for food. Also the greater part of most medicines is evacuated from the system in this way. Oil of turpentine and the natural balsams impart to the urine a smell of violets. Cantu has shown that the urine contains mercury and becomes alkaline after the rather free use of mercurial ointment. Such urine, when cool, forms a sediment which after drying and distillation with powdered charcoal, yields amongst other products, globules of metallic mercury. After the internal use of nitre, ferro-prussiate of potassa, and other salts, the urine is found to contain them, and it has sometimes been observed that the urine of those who employ large quantities of preparations of iron becomes bluish or greenish from the presence of a small quantity of prussian blue, recognised by its yielding oxide of iron after ignition. Wöhler has performed some interesting examinations on the matters which may again be found in the urine of men and dogs. After swallowing oxalic or tartaric acid the urine deposits, when cool, a white crystalline powder which consists of the

salts of lime with these acids, and of which still more is deposited when the urine is mixed with a solution of chloride of calcium. Tartaric acid, moreover, seemed to render the urine considerably acid. It was known before that citric and malic acids have the same properties. After the use of infusion of galls, the urine gave dark-coloured precipitates with the salts of iron. Benzoic acid* and succinic acid also reappeared in the urine. Iodide of sodium and iodide of ammonium were found after the use of iodine. The alkaline carbonates, borates, silicates, chlorates, and nitrates were always found in the urine, so that either the salt itself or the acid could be recovered. Ferro-prussiate of potassa and sulpho-cyanide of potassium were easily discovered by their reaction with the salts of the sesquioxide of iron. The red ferro-prussiate passed over into the urine as ordinary ferro-prussiate. Even sulph-hydrate of potassa was partially found unaltered; the greater part, however, was converted into sulphate of potassa. On the other hand, Wöhler found that both in dogs and men the neutral salts of the vegetable

* It is possible the benzoic acid is hereby converted into hippuric acid. At least the beautiful prismatic crystals of the acid which I obtained from the urine of a dog which had taken benzoic acid resembled more hippuric than benzoic acid in their external appearance. This would easily explain the occurrence of hippuric acid in the urine of herbivorous animals, since it might be supposed that the benzoic acid in their food was converted during digestion into hippuric acid.

Wöhler.

acids with potassa and soda were decomposed by the vital processes, so that the alkali passed off with the urine as a carbonate, and after the abundant use of them the urine became so alkaline that it effervesced with acids. It happens, therefore, very frequently, that after the free use of certain fruits, for instance, apples, cherries, strawberries, raspberries, &c., the urine becomes alkaline, because these fruits contain malate and citrate of potassa which are decomposed by the vital processes. This circumstance explains the known fact that the continued use of such fruit has been found efficacious in lithic acid gravel affections.

For the rest experience has shown that most of the colouring matters of plants pass over into the urine, as for instance, the red colour of berries, particularly of cherries, mulberries, the fruit of the cactus opuntia, &c., (from the use of which the urine will become red by acids and green by alkalies,) hematoxylin, alizarin or madder-red, (whereby the precipitate of lime from the urine by ammonia becomes pink,) indigo, rhubarb, several varieties of tannic acid, (whereby the urine is coloured green or black by the salts of the sesquioxide of iron,) several aromatic vegetable substances, as oil of turpentine, oil of juniper, volatile oil of valerian, oil of onions, the aromatic substance of castor, the narcotic of opium, &c.

On the other hand the matters which do not

pass into the urine are:—mineral acids, which never make the urine more acid than it is, alcohol, ether, camphor, empyreumatic animal oil, musk, the colouring matter of cochineal, litmus, sap-green (from the fruit of *rhamnus cathartica*,) and alkanna. So also iron in its oxidized combinations, and the preparations of lead and bismuth.

ACCIDENTAL INGREDIENTS OF THE URINE IN DISEASES.

Urine in fever.—In the first stage of fever, ordinarily beginning with a chill, the perspiration is interrupted and the urine contains more than its usual quantity of water, because that which otherwise would have been given off by the skin, is now removed by the kidneys; on the farther development of the fever, accompanied by heat and increased pulse, the urine becomes darker than usual, but still deposits no sediment. Its free acid is diminished in proportion as the colour deepens, and it now begins to react with chloride of mercury, which produces no precipitate as long as the urine is sufficiently acid. The urine becomes more concentrated as the fever increases; it now begins to yield a precipitate with alum and at last with nitric acid. Both these re-agents show an increased quantity of albumen in the

urine. When the fever passes away after the lapse of a certain number of days, say after the seventh, the free acid reappears at once, its colour becomes lighter and it appears cloudy on cooling. Physicians call this the crisis by the urine; the sediment contains nothing peculiar from the disease, but only a little more red colouring matter than usual, and sometimes a little nitric acid in an unknown combination. In every paroxysm of intermittent fever the urine passes through these three conditions, and the colouring matter has the hue of carmine. Fromherz and Gugert observed that in *lenta nervosa*, a copious, reddish yellow precipitate of lithic acid, with but little colouring matter of the urine was continually deposited; there was but little urea present, though there was much phosphate of magnesia and the other ingredients in usual quantity.

Without doubt much might be learned from examination of urine in fevers, of great importance to the physician in diagnosis and treatment, especially if the examination could be reduced to the use of tests easily applicable. But this is scarcely to be hoped so long as we know so little of the organic constituents of the urine in its healthy state.

In *anasarca* arising from general debility, the serous fluid is also separated by the kidneys and the urine becomes albuminous. It will then give a precipitate with chloride of mercury even when

it has an acid reaction. In the farther progress of the disease the kidneys secrete an albuminous solution; it can then be precipitated by alum, and, in the still farther progress of the disease, by nitric acid, and at last it coagulates by heat. As the albuminous matter increases, so the ordinary ingredients of the urine diminish, and, finally, altogether disappear. Albuminous urine also occurs with deficiency of urea in chronic affections of the liver, complicated with dyspepsia; also towards the termination of all emaciating diseases that are accompanied with hectic fever.

In a peculiar affection of the kidneys described by Bright, a portion of the serum of the blood is secreted with the urine, which gradually increases, though it ceases again before the sickness terminates in death. The urine contains so much albumen that it congeals by a temperature of 150° F.

Fibrin has sometimes been found in urine, which then coagulates or deposits a coagulum shortly after its evacuation. The urine sometimes contains globules of blood in solution; it is then called bloody urine, from its appearance.

Urine, containing *milk*, has been observed several times. Such urine separated cream, coagulated by heat, and the coagulum had the properties of casein; ether extracted fat from it. This kind of urine has been secreted by both men and women, in consequence of unknown causes, and

even sometimes without any manifest indisposition.

From severe vomiting (occasioned by headach, schirrus of the stomach, &c.) the urine is sometimes turbid, looks milky, and deposits a white sediment. On the filter it becomes slimy, and on drying it is first yellowish and transparent, afterwards white and pulverulent. The addition of water renders it again slimy; caustic potassa dissolves the mucus from it and leaves the phosphate of lime; chlorohydric acid dissolves the phosphate, rendering the mucus at first transparent, and then dissolving it. Fromherz and Gugert found in the urine of a person with black vomit, who suffered from schirrus of the pylorus, perfectly similar mucus mixed with phosphate of lime; the urine was alkaline from the presence of carbonate of soda and ammonia; it contained much urea, but no lithic acid.

In *rheumatism* the urine is generally acid, depositing sediment oftener than in health; but in the fever accompanying the paroxysms the acid of the urine decreases and disappears as it does in other fevers. The quantity of lithic acid is also considerably increased in rheumatism, which might be anticipated from the fact of the earthy concretions, found in the joints, consisting of lithate of soda with some lithate of ammonia.

In *jaundice* the urine has a yellow colour, from admixture of the ingredients of the bile;

it has also been seen decidedly green from dissolved biliverdin. It is easily recognised from the changes it undergoes when mixed with an equal volume of nitric acid. With chlorohydric acid, it becomes green or brown according to the modification in which the colouring matter of the bile exists in the urine. In diseases of the liver the urine leaves a yellow stain on linen when dried. Sometimes it is turbid and leaves yellow flocculi on the filter, chiefly composed of the colouring matter of the bile, the solution of which in potassa gives the ordinary reaction with nitric acid. Gmelin and Tiedmann found that such urine gave a green precipitate with sulphate of copper, while with sulphate of protoxide of iron, chloride of tin, chloride of iron, acetate of lead, nitrate of the protoxide of mercury and chloride of mercury, the precipitate was yellow.

In *cholera morbus* the urine is very variable. Vogel has published some examinations of it. In the first twenty-four hours he found the colouring matter of the bile, which first turned green and then red, on the addition of nitric acid. He afterwards found that the salts of lime and of magnesia were absent, that there was very little chloride of potassium or sodium, more than the ordinary quantity of sulphates, and phosphoric and lactic acids in abundance. It coagulated slightly when boiled, and deposited a little albumen. With

nitrate of protoxide of mercury it yielded a light gray precipitate, which soon became black from the presence of albumen with its sulphur. A day or two afterwards the albumen and the colouring matter of the bile disappeared, but the salts of lime, chloride of sodium, &c., were again present.

The urine is often altered after *colic*. L. Gmelin found it clear but browner than usual. It contained the brown colouring matter of the bile, which could be precipitated by a small portion of chlorohydric acid. By the addition of more acid it was again dissolved without yielding any farther precipitate. The precipitate was recognised as colouring matter of the bile from its property of dissolving in caustic potassa, with a brown colour, which turned bright red on the addition of nitric acid. It did not exhibit the ordinary change of colours, from green to blue and red, but Gmelin observes, that he has often noticed this in the colouring matter of the bile after it had been passed with the urine. On the addition of much nitric acid to this urine it assumed a red colour; a smaller quantity of the acid precipitated the brown matter which being dissolved in potassa and nitric acid added, the solution did not become so bright red as when it was precipitated first by chlorohydric acid. This urine also deposited the ordinary red sediment after some hours rest.

In *spasmodic or hysterical complaints* the urine

sometimes becomes altogether colourless and as clear as water. According to Rollo, the urea and organic ingredients are entirely wanting, and only the usual salts are found in it.

The secretion of *blue urine* has been several times observed; the colouring matter suspended in it was not the ferro-prussiate of iron. Garnier and Delens found it slightly soluble in water; neither acids nor alkalies altered the colour, but nitric acid destroyed it. Braconnot found the blue matter tasteless, inodorous, darker than ferro-prussiate, and in extremely minute division. By heat it gave carbonate of ammonia and empyreumatic oil. It was slightly soluble in water and boiling alcohol; the latter solution assumed a greenish colour and deposited on cooling a little dark blue, almost crystalline powder. By evaporating the alcohol the blue matter remained soluble in acids, which left some fatty matter undissolved. This colouring matter is soluble in acids, and even in certain vegetable acids such as oxalic and tannic acids, which also redden it. When a saturated solution of it in dilute sulphuric acid was evaporated, it had the colour of carmine. The solution in water was brown, but it became red by evaporation. Acetic acid dissolved very little of it; the solution was yellowish brown, but after evaporating the acid the colouring matter remained of an unchanged blue. By saturating the red solutions in the acids with an alkali, they resume their red colour, while the colouring matter

is again precipitated. Caustic potassa dissolved but little of it, and carbonic acid almost none. The urine from which this blue colouring matter was separated by filtration, deposited, when warmed, a new portion of colouring matter, so dark that it seemed almost black, but otherwise having the same properties.* According to Spangenberg the blue colouring matter, deposited from a specimen of urine in combination with the ordinary sediments from which it could be extracted by boiling alcohol, amounted to about one-fourth of the weight of the sediment. The solution was blue and by evaporation the colouring matter remained without the least appearance of crystallization. It was also soluble in boiling ether. Concentrated sulphuric acid dissolved it with a blue colour, but chlorohydric acid produced no effect on it even by ebullition. By nitric acid it became yellow, lost its peculiar properties and was converted into picrin-nitric-acid. It was insoluble in caustic alkalies and their carbonates. By incineration it left a small quantity of a white ash consisting of phosphate of lime. This examination shows that the matters which colour the urine blue are not always of the same kind.

A *black colouring matter* has also been ⁴found in the urine. Marcet has described the urine of a child, which contained neither lithic acid nor urea, but with a colour occasionally as black as

* Braconnot considers this colouring matter to be a peculiar base and calls the one cyanourine, and the other melanourine.

ink, or becoming so on the addition of an alkali. By acids it was first apparently unaltered, but after a while it deposited dark flocculi and became clearer. The dark precipitate was insoluble in water and alcohol, but soluble in sulphuric and nitric acids with a black colour, and could again be precipitated from them unaltered by the addition of water. On the other hand it dissolved in caustic alkalies and their carbonates with a dark colour, and was again precipitated by acids. The solution in ammonia left, by evaporation, a shining, dark brown, cracked mass, which again dissolved in water, retained ammonia in combination and gave it off on the addition of potassa. With metallic salts it gave brown precipitates. Proust, who examined it chemically, considered the black colouring matter as a weak acid, and called it melanic acid. It has great resemblance to the black, pulverulent substance, insoluble in alcohol, which, according to Proust, is produced by the reaction of concentrated acids on the extractive matter of the urine.

In the sediment of the urine a black substance has sometimes been found, which is called Hematin; after treating the sediment with chlorohydric acid, which extracts the phosphate of lime, and then dissolving it in alcohol, mixed with sulphuric or chlorohydric acid, it may be precipitated by the alkaline carbonates, added in quantity exactly sufficient to saturate the solution. Hematin can easily be recognised from these properties. It

may also be extracted from the sediment by alcohol mixed with a few drops of caustic ammonia; after evaporation of the alcohol it is recognisable by the quantity of oxide of iron which it affords by incineration.

In *diabetes* the urine contains sugar instead of urea, from whence it has a sweet taste. In the beginning of this disease no other symptoms are observed than that the urine is secreted in larger quantity than usual, and that the appetite proportionally increases; however, an alteration soon occurs, from which all water taken with the food passes into the urine. The perspiration is interrupted, and the skin becomes dry and rough. The more the urine increases in quantity and sweetness the more concentrated it becomes, and its specific gravity has been found as high as 1.050, and even higher; Bouchardat found it as high as 1.074. In proportion as the sugar increases, the quantity of urea diminishes, but it always reappears when the sugar decreases.

Diabetic urine is of a pale straw colour; it has a sweet taste, and a smell like whey. The inorganic salts are found in it, in their ordinary relative proportion, but in more dilute solution. Towards the end of the disease, when hectic fever supervenes, the urine becomes albuminous, and, therefore, easily passes into vinous fermentation. It may, however, always be easily fermented by yeast, after which it will give much alcohol by distillation.

The quantity of urine sometimes increases to so great an extent, that instances occur in which eleven or twelve quarts of water have been passed in twenty-four hours, and this has continued for months. It is accompanied with an unquenchable thirst; but as the drink soon finds its way through the kidneys, taking up a new quantity of the substance of the body, it happens in this disease that for a long time more passes away by the urine than corresponds to the daily food of the patient, until he finally succumbs. Henry has calculated from experiments that an English wine-pint of diabetic urine of sp. gr. 1.020, evaporated to dryness, yields a residue of 382.4 grains, which increases 19.2 grains for every unit by which the specific gravity is increased until it has reached 1.050; so that when it has a specific gravity of 1.021, it leaves a residue of $382.4 + 19.2 = 401.6$ grains; and when 1.050 sp. gr., the residue is 958.4 grains, which corresponds to 43.559 grammes of solid matters to one litre of urine of 1.020 sp. gr.; and for every unit the specific gravity increases 2.1871 grammes.

When the urine is evaporated and treated with alcohol, the sugar and extractive matter, soluble in alcohol, are dissolved. After sufficient evaporation, the sugar crystallizes from this solution in small granular crystals, like sugar of grapes. Sometimes, however, merely a sweet syrup is obtained, which does not yield crystals. It has not yet been ascertained whether there exists an un-

crystallizable variety of diabetic sugar, or whether it is caused by containing so much deliquescent extractive matter that its water prevents the crystallization of the sugar. At all events it may be easily determined by destroying the sugar by fermentation, and evaporating the fermented liquid, whereby the extractive matter is separately obtained. The opinion at one time prevailed that this sugar constituted a distinct species, but Prout has placed it beyond all doubt that it is the same sugar which in vegetable chemistry is called grape sugar; with which it agrees in all its chemical properties, and also, according to Prout's analysis, in its composition. Its properties and composition have also been since examined by other chemists, lately by Peligot, and by Erdmann; and all examinations prove its identity with grape sugar, and that its formula is $C^{12} H^{12} O^{12}$, or simply $C^6 H^6 O^6$.

It is no easy matter to separate the sugar in its pure state. The urine is evaporated in a water-bath to the consistence of honey, the remainder treated with alcohol of 0.833 as long as any substances are dissolved by it. The alcoholic solution is then evaporated to the consistence of a syrup, which is to be put in a cool place for crystallization, where, generally in a few days, sometimes not before a week or ten days, it is converted into a granular mass. This mass is put in a cool place after it has been laid on folds of bibulous paper, and covered by a glass receiver, in which a moist-

ened sponge is suspended. The extractive matters deliquesce and are absorbed by the paper, which, with exception of the sheet on which the sugar is lying, may be occasionally changed. When the paper absorbs no more, the mass is to be crumbled, pressed between fresh bibulous paper, and left for a few days in a warm place under the receiver with the moistened sponge. Finally, the sugar should be powdered and washed with anhydrous alcohol. It is then to be dissolved in water and crystallized.

Another method is to precipitate the solution in alcohol of 0.833, with subacetate of lead added in small portions as long as any separation occurs. The liquid should be well shaken after every addition of the subacetate. The mixture is then filtered, the precipitate washed with a little alcohol, the spirituous solution treated with sulphuretted hydrogen, filtered from the precipitated sulphuret of lead, and is then evaporated to the consistence of honey. When the sugar has been separated by crystallization, the urea, acetic acid, and other substances which it retains are extracted by anhydrous alcohol. By this operation the sugar is obtained both more speedily and more colourless.

It is very important to the physician to have an easy way of detecting sugar in urine supposed to be diabetic. The ordinary test is very easy; it consists in adding two tea-spoonsful of ferment to three or four ounces of urine, and placing the mix-

ture in a temperature of about 70° F. In urine containing sugar fermentation soon takes place, while none occurs when no sugar is present.

Runge gives another equally easy and still quicker test. A few drops of the suspected liquid are placed on a saucer and held over the mouth of a tea-kettle containing boiling water; as soon as the urine is dried a few drops of dilute sulphuric acid are added, consisting of one part of concentrated acid to six or eight parts of water, and then heated gently for a few moments. If the urine contains sugar the spot soon turns black, otherwise it has an orange colour. This reaction is so delicate that when one part of sugar is dissolved in one thousand parts of healthy urine the spot is blackened; and with one part of sugar to two thousand of urine it becomes sufficiently dark to yield a distinct proof of the presence of sugar.

Hünefeld gives another less applicable test. One ounce of the urine is mixed with a few drops of a solution of chromic acid and placed in the light. It soon changes its colour, passing from brown to green. This reaction does not occur in any other than diabetic urine. Neither is it caused by the sugar in the urine, since when grape sugar is dissolved in healthy urine and mixed with chromic acid, the mixture does not turn green.

Hünefeld has also attempted to prove that diabetic urine contains an extractive matter peculiar to this disease, and which he obtained from the

precipitate by subacetate of lead, by treating it with water and sulphuretted hydrogen. But this extractive matter is mixed with several other substances as we have seen before, and its reactions do not essentially differ from those obtained by the extractive matter from healthy urine. This substance, therefore, must be subjected to a new examination for the purpose of comparing it directly with the extractive matter of healthy urine.

Lehmann has also discovered hippuric acid in diabetic urine. He extracted it by ether from the concentrated urine. After partial distillation, and spontaneous evaporation of the remainder, he obtained a mixture of extractive matter with crystals of hippuric acid. Experiments performed with these crystals seemed to leave no doubt that they were hippuric acid. They do not seem, however, to be a constant, but only an accidental ingredient of diabetic urine.

I will here quote an analysis by Meisner to show the composition of urine in diabetes. The different portions were obtained at different times from the same individual.

| | | | |
|---|-------|-------|-------|
| Matter soluble in ether; urea, lactic acid, lactate of lime and extractive matter | 0.34 | 0.33 | 0.65 |
| Matter soluble in alcohol; sugar, extractive matter and salts | 7.06 | 3.46 | 5.78 |
| Matter soluble in water; extractive matters and salts | 1.37 | 3.44 | 0.99 |
| Mucus with phosphate of lime and a trace of oxide of iron | 0.34 | 0.31 | 0.46 |
| Water | 91.19 | 92.46 | 92.10 |

A still more concentrated diabetic urine was analyzed by Bouchardat, and gave :

| | |
|------------------------------------|---------|
| Sugar | 13.442 |
| Urea | 0.827 |
| Alcoholic extract | 0.638 |
| Extract soluble in water | 0.527 |
| Salts | 0.869 |
| Mucus | 0.024 |
| Oxide of iron (?) | 0.014 |
| Water | 83.758 |
| | <hr/> |
| | 100.000 |

An analysis still more detailed, has been published by Muller ; he found

| | |
|---------------------------------|---------|
| Sugar | 4.900 |
| Urea | 0.006 |
| Alcoholic extract | 1.420 |
| Watery extract | 0.360 |
| Albumen | 0.029 |
| Mucus | 0.021 |
| Sulphate of potassa | 0.021 |
| Chloride of sodium | 0.054 |
| Chloride of potassium | 0.015 |
| Phosphate of soda | 0.110 |
| Chloride of ammonium | 0.083 |
| Phosphate of lime | 0.028 |
| Silica | 0.004 |
| Water | 93.766 |
| | <hr/> |
| | 100.000 |

These analyses can never be made with sufficient accuracy to be considered any thing more than approximations; it may, however, be seen from them that as sugar increases in the urine,

the latter becomes more concentrated and contains less water.

The disease seems to consist in a mal-assimilation of protein substances, from which in healthy conditions of the body urea is formed, but which in diabetes are converted from unknown causes into sugar, ammonia, and perhaps an azotic extractive matter. We see that protein substances, notwithstanding their nitrogen, may cause the formation of sugar from their reaction with nitric and chlorohydric acids. Chlorohydric acid, for instance, converts protein into ammonia and humin or humic acid, which is the same black substance capable of combining with an alkali, that the acid produces with sugar. Nitric acid yields with protein both xantho-proteic acid, and saccharic and oxalic acids in abundance. Before the disease has made much progress, sugar cannot be found in the blood, any more than urea, wherefore its formation was ascribed altogether to disease of the kidneys. But later experiments on the blood of diabetic patients have proved that when the formation of sugar is abundant, it is also found in the blood. It is said to have been found even to the amount of one per cent. ; in most cases, however, it exists in much less quantity. Bouchardat asserts that the quantity of sugar in the blood is greatest a few hours after eating, and that it is entirely absent in the morning, because the sugar has been separated from the blood during the night. In order to detect it the fresh blood is

coagulated by admixture with strong alcohol, the solution filtered and the coagulum washed. The alcoholic solution is to be evaporated to dryness, the residue treated with alcohol of 0·833, the solution decanted and left to spontaneous evaporation. A syrup is now obtained which, after standing a few days in a cool place, gives granular crystals of grape-sugar. It may more easily be tested for sugar by the method of Runge; according to which it is only necessary to evaporate a few drops, and treat the remainder with a few drops of dilute sulphuric acid, in the manner before mentioned.

This disease is considered incurable, and it is in fact very seldom cured. The best treatment seems to consist in placing the patient on a strictly animal diet, so as to deprive the kidneys of all such matter as they could easily convert into sugar. According to Henard the urine becomes albuminous before the sugar diminishes, and, therefore, before the urea reappears; but afterwards it ceases to be albuminous. The progress of convalescence is easily ascertained by observing whether the quantity of urea increases.

There is another kind of diabetes called *diabetes insipidus*, in which the urine does not taste sweet, but its quantity is unnaturally increased. In this complaint urea ceases to be formed, and the urine leaves on evaporation a brownish yellow syrup with a faint acid reaction, without any disposition to crystallize. Alcohol of 0·833 dissolves the

greater part of it, and leaves on evaporation a yellow deliquescent extract, which apparently exactly resembles the substance which alcohol of the same strength extracts from a concentrated solution of flesh. Even the part insoluble in alcohol is an extractive matter. Bouchardat has published an analysis of urine in this disease. He found:

| | | |
|--|--------|--------|
| Extractive matter soluble in alcohol | 1.321 | 1.837 |
| Extractive matter soluble in water | 0.427 | 0.548 |
| Urea | — | 1.431 |
| Mucus and phosphate of lime | 0.012 | 0.036 |
| Salts soluble in water | 0.524 | 0.927 |
| Lithic acid | 0.024 | 0.064 |
| Water | 97.692 | 95.157 |

It is to be observed that in this disease also, urea is sometimes present and sometimes absent.

Urinary concretions, or calculi and gravel.—When insoluble substances are deposited from the urine while yet in the body, they form concretions in the urinary passages which, from the earliest times, have been the subject of speculation as well as of examination. From Galen to Paracelsus the formation of these concretions was referred to supernatural causes. Van Helmont very correctly compared their formation to the crystallization of tartar from wine. Since his time they have been treated of with very different views by many authors, amongst whom may be mentioned Hales, Boyle, Boerhaave, and Slare. The first correct view of their nature was given by the analysis of

some calculi by Scheele in the year 1776; by which he discovered lithic acid, which he afterwards found in the urine. But Scheele meeting with no other than lithic acid calculi, concluded that they were all composed of this substance. Bergmann then found a calculus consisting of earthy phosphates, whence it appeared that the composition of these concretions might be very different. In the year 1797, Wollaston described the following five different kinds:—lithic acid; phosphate of lime; a mixture of the latter with double phosphate of magnesia and ammonia (fusible calculi;) pure double phosphate of ammonia and magnesia; and oxalate of lime (mulberry calculi.) Fourcroy and Vauquelin a short time afterwards invited physicians to send them specimens of calculi for examination. They collected in this way 600 specimens, which enabled them to examine a great variety. They found the same substances as Wollaston, and moreover lithate of ammonia, and in two specimens they found silica. The author of their common treatise has been properly censured for affecting ignorance of the results of Wollaston, which were published almost three years before in the transactions of a learned society, which the French Academy of Sciences, beyond all others, could not be ignorant of. Proust afterwards found human calculi containing carbonate of lime. His accuracy was at first doubted, because Fourcroy and Vauquelin had not found this substance, but later experience has substantiated

it. Wollaston then discovered in the year 1810 a new ingredient in calculi, which he named cystic oxide. A. Marcet discovered another substance which he named xanthic oxide; and afterwards, also, a calculus of fibrin of the blood. Lindebergson discovered lithate of soda and carbonate of magnesia as ingredients in a calculus.

The formation of urinary concretions is caused by the secretion of insoluble matters in the urine, in greater proportion than can be kept in solution by it; or by the quantity of free acid in the urine becoming too little to retain the earthy phosphates in solution; or by a sickly disposition of the body giving rise to the secretion of uncommon and insoluble substances which deposit immediately, such as oxalate of lime, &c. The manner in which they deposit is various. Sometimes they precipitate in the state of powder and pass out with the urine which is rendered milky and turbid; or they are formed immediately in the pelvis of the kidneys, adhering to the inner surfaces, at first, but afterwards becoming loose, they pass with more or less colic-like pains along the ureters into the bladder, from which they are evacuated with the urine in the form of gravel. But if unfortunately a grain or small calculus should remain in the bladder it becomes a nucleus for the slow deposition of the insoluble ingredients of the urine, of which it now causes the precipitation even should the urine contain them in no greater quantity than it would, under ordinary circumstances,

retain in solution. Now by variation in the diet at different times, the quantity of one or other of the insoluble matters is increased; this is deposited on the calculus which is thus formed of layers of different substances; and by continually increasing in size at last gives rise to inflammation and disorganization of the bladder, which causes the death of the patient. This is a brief history of calculus disease. They are called renal calculi as long as the disease merely deposits gravel in the kidneys, and vesical calculi when they are formed in the bladder by deposition on a nucleus. These nuclei ordinarily consist of small concretions derived from the kidneys; instances, however, occur where the nucleus consists of foreign substances introduced from without the body.

We will now briefly give a more detailed description of these concretions. They may be divided into three classes. *a.* Pulverulent precipitates. *b.* Deposites of small crystals. *c.* Calculi of larger size.

a. Pulverulent sediments, passing with the urine and rendering it turbid.—These may consist of, 1st. *Lithic acid*; it is then either yellow or lateritious like the ordinary sediment from cooling urine. 2. *Phosphate of lime* mixed with double phosphate of ammonia and magnesia together with much mucus. On the filter it looks like mucus, but it becomes earthy and pulverulent when dry, and then feels soft to the touch. Dilute acids extract the earthy salts, but leave the mucus. The urine

depositing this sediment is always alkaline, and contains carbonate of soda and ammonia. I once had an opportunity of observing a case of this kind: phosphoric acid was administered to the patient in increasing doses, without rendering the urine more acid; but at last the medicine caused dysentery; the urine then became acid, and clear, and deposited lithic acid. This condition ceased with the dysentery; but the formation of sediment and the alkaline reaction of the urine could not be prevented afterwards by the continued use either of phosphoric or acetic acid. This patient gradually emaciated, and finally died. 3. *Mucus* unnaturally increased by catarrh of the bladder. In appearance this resembles the former, but differs from mucus containing the earthy salts, by becoming greenish yellow and transparent when dry, and by the acidity of the urine.

b. Crystalline sediments or gravel.—The substances which are deposited more easily than all others from the urine in small crystals without agglutination to larger masses are, 1st. *Bilithate of ammonia* which occurs in small, shining, reddish, or sometimes yellow, well defined crystals. 2d. *Oxalate of lime* in small, light yellow, green, or brownish-gray, granular crystals. 3d. Double phosphate of ammonia and magnesia in small white and soft crystals. More rarely gravel has been found composed of other substances, for instance of cystin and xanthic oxide; perhaps these are not so rare as is generally believed, but eva-

coated gravel is seldom examined, and these matters often may have existed without being recognised. To those concerned it is of importance to be able to distinguish between gravel which is formed before evacuation and such as forms by cooling. This is easily done by draining the urine through linen, as this retains the gravel which passes from the bladder.

c. Calculi.—Their colour varies according to their ingredients. They are white, gray, yellow, or brown. Their surface is either earthy, smooth and polished, occupied by mamillary excrescences, or covered with small projecting crystals. As long as they are moist they retain the smell of urine. According to Marcet their specific gravity varies between 1.2 and 1.9. Their form is sometimes determined by the part on which they were lying, and when there are several present, their surfaces generally become smooth and flattened by trituration against each other; they are, however, for the most part oval, and their size varies from that of a hazelnut to that of a hen's egg. Calculi have been found in the bladder weighing more than three pounds. Their transverse section gives the most interesting view of their general characters. Their inner structure is made apparent by cutting through their centre with a fine, broad, and sharp saw, and grinding and polishing the new surfaces with water and the powder formed by the saw. Ordinarily, there is a nucleus in the centre, which has been sur-

rounded by other substances in alternating layers of different thickness, so that calculi have been found consisting of layers of all the ordinary ingredients of urinary calculi. Many, however, consist entirely of the same substance which has been deposited in layers of different thickness, and which often scale off from each other. I will now treat separately of the different substances which compose the calculi.

1. *Lithic acid* is the most common ingredient of urinary calculi. They have a reddish brown, or brownish yellow colour; sometimes they are pea-yellow, less often white. Their surface is partially smooth and partially covered with small mammillæ. The transverse section exhibits thin, concentric layers, and the fracture is either imperfectly crystalline or earthy. Lithic acid never exists in its pure state in urinary concretions, but is always united with the same colouring matter which accompanies it in the sediment of the urine, and from whence they derive a yellow or mahogany colour. Ether nearly always extracts from these, as it does from all kinds of calculi, a portion of the same kind of fat that ordinarily occurs in animal fluids. Part of the yellow colouring matter may be extracted by acetic acid, which then becomes yellow. Besides this they always contain either albumen or mucus, and it is difficult to say which of the two it is in any particular case. If a calculus of this kind be dissolved in caustic potassa, and the lithic acid precipitated by the

addition of chlorohydric acid in excess, and washed on a filter, the wash-water, as soon as the excess of chlorohydric acid is removed, dissolves a substance which again precipitates by mixing with the previously filtered acid solution. If this water be collected separately and mixed with chlorohydric acid the precipitate behaves exactly like the neutral combination of this acid with fibrin or albumen, and its solution in water is precipitated by ferro-prussiate of potassa. This reaction also belongs to the mucus of the bladder, and it therefore seems to follow that this substance unites with lithic acid in a combination analogous to that in which it is taken up by chlorohydric acid. All calculi of lithic acid contain a small quantity of lithate of potassa, soda, ammonia, and sometimes lime; they, therefore, leave a little ash, after incineration, consisting of the alkaline carbonates and carbonate of lime. Sometimes they also contain a greater or less admixture of the earthy phosphates. The chemical characters by which calculi of lithic acid are recognised, are the following: they are soluble in caustic potassa, yielding only a slight ammoniacal odour; but a residue of gelatinous phosphate of lime is often left, which, when its quantity is small, dissolves in an excess of potassa. This solution yields with acids a gelatinous precipitate which soon collects into a granular powder. These calculi dissolve in nitric acid very easily. The solution is yellowish, and becomes red by evaporation at a moderate heat.

The residue is again soluble in water, giving a colourless solution which turns red by evaporation. This test is easily made on a watch-glass or piece of porcelain with a small piece of the calculus not larger than a mustard seed. When the acid is added in excess, or too great heat is employed in the evaporation, the red colour is destroyed and changed to yellow; on this account Jacobson prescribes the evaporation of the solution in nitric acid nearly, but not perfectly, to dryness over a lamp; the watch-glass is then to be inverted over another containing a few drops of caustic ammonia and gently heated. The ammoniacal fumes saturate the nitric acid, and the red colour immediately appears in the upper glass. The easiest way of discovering foreign admixtures in calculi of this kind, is to calcine a small portion of it on platinum foil before the blow-pipe. At first the outer flame is applied which produces the smell of burnt horn and strong prussic acid odours, while the calculus continually diminishes in size. The residue at last takes fire and burns spontaneously with much splendour, even after the cessation of the blast. Calculi of pure lithic acid leave only a small trace of ash. If they give much ash which is not alkaline they were mixed with earthy phosphates. If, on the contrary, the ash is strongly alkaline, but insoluble in water, they either contained lithate of magnesia or oxalate of lime which has been burnt caustic.

2. *Lithate of soda*, with traces of lithate of

potassa, has never yet been found as the sole ingredient of urinary concretions. Lindbergson found it to be an ingredient of a calculus, of which the composition will be given hereafter.

3. *Lithate of ammonia* occurs, though rarely as the sole ingredient of urinary calculi, and more frequently in children than in adults. They are generally small in size, of a white or gray colour like clay, with a smooth, sometimes tuberculated surface, consisting of concentric layers and having an earthy fracture. Some time after Fourcroy and Vauquelin had proved the existence of this kind of calculus, W. Brande declared it to be an error, asserting that lithate of ammonia never occurred in urinary concretions. The ammonia generated by caustic potassa from calculi, according to him, derives sometimes from an admixture of double phosphate of ammonia and magnesia, but chiefly from the ammoniacal salts and urea of the urine with which the calculi are always saturated when first extracted, and of which a certain quantity always remains after drying. Prout, however, soon proved the error of Brande's assertion, and was confirmed afterwards by several others. The calculus is reduced to powder and washed with cool water to extract the remaining urine; it is then boiled in a large quantity of water which dissolves the lithate of ammonia and again deposits the greater part of it in crystals. The residue obtained by the evaporation of this solution is treated, when cool, with chlorohydric

acid, whereby the lithic acid is separated, and by evaporation of it, sal-ammoniac remains behind. Should the stone consist altogether of lithate of ammonia much water will be required for its solution, and it is, therefore, preferable to treat it at once with chlorohydric acid. A few drops of this solution is tested with caustic ammonia to discover the presence of double phosphate of ammonia and magnesia. The rest forms by evaporation a saline mass, in which the presence both of ammonia and soda may be shown by subliming a portion of the dry mass in a test tube: sal-ammoniac, impure from destroyed animal matters sublimes, and a portion of chloride of sodium mixed with carbon generally remains at the bottom of the tube. Lithate of ammonia may likewise be easily recognised by its yielding ammonia when treated with a solution of caustic potassa. But this test is liable to error because the same will occur with double phosphate of ammonia and magnesia. The doubt, however, may soon be removed by the addition of a little water, which in the case of lithate of ammonia dissolves the whole, while in the latter case the magnesia remains undissolved. The behaviour of these calculi towards nitric acid and heat, is the same as those of lithic acid.

4. *Lithate of magnesia* forms the rarest kind of calculi, both because the magnesia constitutes so small a portion of the ingredients of the urine, and because its salt with lithic acid is rather soluble. Sharling found it to form the prevailing ingre-

dients of two calculi, in which it was associated with lithate of ammonia. The presence of this salt in a calculus is easily discovered by boiling the powder in water, which dissolves the salts both of magnesia and ammonia. The solution is treated with chlorohydric acid, which precipitates the lithic acid, and the remaining solution is to be evaporated to dryness in a water-bath. The residue is then moistened with a little concentrated chlorohydric acid and the greater part again evaporated from it. Anhydrous alcohol then dissolves the chloride of magnesium, leaving the chloride of ammonium, of which the weight may be estimated. The magnesia is obtained from the alcoholic solution by admixture of a little carbonate of potassa, evaporation to dryness in a platinum crucible, ignition of the remainder to commencing redness, and extracting the excess of potassa by water. If it is only desired to test it, a little of the calculus is boiled with water, and the boiling solution mixed with a few drops of caustic potassa, which precipitates the magnesia.

Lithate of lime is found only in small quantities in calculi consisting chiefly of lithic acid.

5. *Lithous acid*, A. Marcet's *xanthic oxide*.—It forms a rare variety of calculus. The first was discovered by Marcet; it weighed eight grains and had a brown colour. When a portion of it was dissolved in nitric acid and the solution evaporated to dryness, the residue was not red as from lithic acid, but yellow, whence Marcet derived the name

from the Greek word *χρῆμα*, *yellow*. Stromeyer afterwards found a larger calculus of this kind which Langenbeck had extracted from a young farmer's boy in the hospital at Göttingen. Although Marcet had given a description of this new substance, we owe our knowledge of it principally to an examination which Liebig and Wöhler made of a portion of the above-mentioned calculus extracted by Langenbeck. The changed name, under which it is here treated of, is founded on an elementary analysis of it performed by them.

The surface of a lithous acid calculus is partly light brown, smooth and shining, partly whitish, dull and earthy. Its fracture has a brown flesh-colour. It consists of concentric scaly layers having neither a crystalline nor fibrous appearance; it assumes a waxy lustre by rubbing, and has nearly the same hardness as a calculus consisting of lithic acid. The nucleus consists of the same substance. It dissolves in nitric acid by heat without the slightest effervescence, and the solution leaves by evaporation in a water-bath a yellow residue, which does not become red either by stronger heat or by the fumes of ammonia. It does not fuse by heat; it is destroyed by dry-distillation, yielding first the odour of prussic acid and then of burnt horn, exactly like the odour of the fumes of lithic acid, and a carbonate of ammonia sublimes which contains no cyanate of ammonia nor urea. Caustic potassa dissolves it when digested with it in a state of fine powder. The so-

lution has a dark brownish yellow colour with a tendency to green. By passing carbonic acid through the solution till the potassa is saturated, the lithous acid is precipitated in the form of a white powder, free from potassa; which when washed and dried, agglutinates to lumps of a pale yellow colour, which take a waxy lustre when rubbed.

Lithous acid has the following properties. It is without odour and taste; it is decomposed by heat without fusion, and burns away without residue; it is insoluble in water, alcohol, and ether, and soluble in nitric acid without effervescence, though less so than lithic acid; the residue, after evaporating the solution, is lemon yellow and soluble in water with a light yellow colour; it consists of the altered products from lithous acid. The solution in nitric acid acquires an orange colour, when super-saturated with potassa, and sal-ammoniac precipitates a yellow substance from it. Hypochlorite of soda generates a little nitrogen from the solution in potassa, while the colour disappears passing first through blue, brown, and yellow. It is soluble in sulphuric acid; water causes no precipitate from this solution. Chlorohydric and oxalic acids do not dissolve it. Towards bases it behaves as an acid, but is weaker than carbonic acid, which separates it from its combinations with them. Its combinations with potassa and ammonia are very easily soluble in water. Its combination with ammonia leaves by

evaporation a laminated mass, which is bilithite of ammonia. According to Liebig and Wöhler, lithous acid consists of:

| | By experiment. | Atoms. | By calculation. |
|--------------|----------------|---------|-----------------|
| Carbon . . . | 39.28 . . . | 5 . . . | 39.66 |
| Hydrogen . . | 2.95 . . . | 2 . . . | 2.60 |
| Nitrogen . . | 36.35 . . . | 2 . . . | 36.72 |
| Oxygen . . | 21.42 . . . | 2 . . . | 20.82 |

It therefore differs from lithic acid by containing one atom less of oxygen, being $C^s H^s N^s + O^s$; from hence the name lithous acid. It should, however, be observed that so long as its saturating power has not been ascertained by experiment, and it is not known whether it contains water chemically combined, which may be the case, it cannot be considered certain that it is a lower oxide of the radical of lithic acid, however probable this may otherwise be. Considered as lithous acid its atomic weight is 962.216, and its capacity 10.41.

It differs from lithic acid (1) by its greater insolubility in nitric acid and the yellow residue which it leaves after evaporation of this solution, and which does not become red but dark yellow by ammoniacal fumes; (2) by not being precipitated by water from its solution in sulphuric acid, while lithic acid only requires a little water for its precipitation; (3) by a greater solubility in caustic potassa and ammonia. The solution in potassa is not precipitated by the addition of sal-ammoniac,

but by continued evaporation it deposits a powder of bilithite of ammonia. Lithic acid on the contrary is precipitated by sal-ammoniac. Carbonic acid precipitates both from a concentrated solution in potassa, but the precipitate of lithic acid is soluble in luke-warm water, although with difficulty; while the precipitate of lithous acid is altogether insoluble. Lithic acid is dissolved by a dilute solution of carbonate of potassa, but lithous acid is insoluble in it; hence they may be separated when they occur together.

On several occasions, when solicited by physicians to examine gravel evacuated with the urine, I found that the gravel which in every external appearance resembled lithic acid, dissolved with difficulty in nitric acid, and that this solution after evaporation left a yellow residue which did not become red either by heating or by ammoniacal fumes. This gravel was also soluble in caustic potassa; but I always had too little of it to be able to determine with certainty that it was lithous acid. In the meanwhile it is certain that lithous acid must sometimes occur as gravel.

Jackson has stated that he found lithous acid dissolved in the urine of a person affected with diabetes after an injury to the back. The substance which he considered lithous acid deposited from the urine on cooling, with a gray colour; it reddened litmus paper, was slightly soluble in warm water, completely so in nitric acid, from which it was again precipitated by carbonate of

potassa. These reactions, however, do not justify the assumption that it was lithous acid.

6. *Cystin*.—This ingredient of calculi was discovered by Wollaston, who called it cystic oxide, because it was soluble both in acids and alkalies, and resembled in this respect some metallic oxides. But the name *oxide* does not distinguish it as an organic body, since most organic bodies are oxides; nor can the reason assigned for this name be considered admissible. I have, therefore, taken the liberty of differing from its distinguished discoverer in regard to its name.

Cystin, as it occurs in calculi, is a dirty-yellow, transparent, irregularly crystalline mass; but it may be obtained in pure crystals by dissolving it in caustic potassa, and precipitating the boiling hot solution by acetic acid in excess; from this, when it is slowly cooled, cystin crystallizes in six-sided, colourless, transparent plates. It may also be obtained in crystals by the spontaneous evaporation of its solution in ammonia; the plates then have greater thickness, and may be considered as short, regular, six-sided prisms. Cystin has neither acid nor alkaline reaction. It does not melt by heat, but ignites with a bluish green flame and exhales a sharp acid odour, remotely resembling that of cyanogen, but otherwise so characteristic that cystin can be recognised by it alone. It yields by dry distillation an offensive oil, ammoniacal water, and a porous voluminous coal. It is insoluble in alcohol, and almost inso-

luble in water. It is soluble in dilute sulphuric, nitric, phosphoric, oxalic, and chlorohydric acids; by saturating one of these acids and evaporating the solution at a moderate heat, it yields a saline combination of cystin with the acid in diverging needle-shaped crystals, with an acid taste, and little stability, since, for instance, chlorohydric acid evaporates from its combination with it at a temperature of 212° F., and leaves the cystin blackened. When boiled with nitric acid in excess, cystin is decomposed and converted into a dark brown (not red) mass, which remains after evaporation of the acid. Cystin does not combine with acetic, tartaric, or citric acid. It is soluble in caustic potassa and soda, and their carbonates and bicarbonates. It is also soluble in caustic ammonia, but not in its carbonate. Its combination with potassa and soda may be obtained in granular crystals by evaporation, while the combination with ammonia is decomposed and leaves the cystin pure. From its combination with acids it is best precipitated by carbonate of ammonia, and by acetic acid from its combination with alkalis.

Cystin has an uncommon composition. It contains 25½ per cent. of sulphur. It was first analyzed by Prout, who determined its composition rightly in regard to carbon, hydrogen, and nitrogen, but overlooked the sulphur and considered the whole loss as oxygen, in which, therefore, the sulphur is contained. Baudrimont then discovered

and determined its content of sulphur. This gave rise to a new analysis by Thaulow, under the direction of Liebig, whose result I here give with that of Prout:

| | Prout. | Thaulow. | Atoms. | By Calculation. |
|------------|-----------|-----------|---------|-----------------|
| Carbon . . | 29.88 . . | 30.01 . . | 6 . . . | 30.31 |
| Hydrogen . | 5.12 . . | 5.10 . . | 6 . . . | 4.94 |
| Nitrogen . | 11.85 . . | 11.60 . . | 1 . . . | 11.70 |
| Sulphur } | 53.15 . . | 25.51 . . | 2 . . . | 26.58 |
| Oxygen } | . . . | 28.38 . . | 4 . . . | 26.47 |

Marchand found exactly the same quantity of sulphur as Thaulow, and the same quantity of nitrogen as both chemists. The calculated result however differs from the obtained in regard to sulphur by more than one per cent. As long as its capacity of saturation has not been determined by experiments, nothing can be conjectured in regard to the management of its elements.

Lassaigne has described a substance which he found in the calculus of a dog and which he supposed to be cystin, but its composition, as he found it, is so different, that it can scarcely be assumed to be cystin. He states that its solution in ammonia yielded transparent plates by evaporation, and its solution in lime water yielded granular crystals. It formed syrupy combinations with sulphuric and phosphoric acids, but compounds crystallizing in needles with nitric, oxalic, and chlorohydric acids. The sulphate contained 0.896 of its weight of the substance in question; the nitrate 0.969; the oxalate 0.78; and the muriate 0.947.

These quantities do not agree within themselves with the capacities of the acids. Lassaigne found its composition to be as follows: carbon, 36·2; hydrogen, 12·8; nitrogen, 34·0; and oxygen, 17·0. This analysis differs so considerably from the foregoing results, that it cannot be supposed that the substance analyzed by Lassaigne was cystin.

Calculi of cystin contain no other ingredients, at least it has been found so with those extracted from man. Their colour is yellowish, their surface smooth and apparently crystalline, the fracture exhibits an aggregation of small crystals of resinous lustre, with rounded edges. They are recognised by the behaviour peculiar to cystin before the blow-pipe on platinum foil, also by their solubility in caustic ammonia and chlorohydric acid, and by the form of the crystals of the combination remaining from the slow evaporation of the ammoniacal solution. Since Wollaston's account of it, cystin has been found by Marcet, Stromeyer, Buchner, Robert, Walchner, and Taylor. The latter found amongst 129 calculi in the collection of Bartholomew's hospital, at London, two very large calculi of cystin, the greater of which weighed 720 grains.

7. *Phosphate of lime* very seldom occurs alone, and in neutral combination. Wollaston is the only one who has discovered calculi of this kind. According to his account their surface is light brown and polished. The transverse section exhibits lamina lying regularly over each other,

which can easily be separated, and the calculus divided into concentric shells. The fracture of each layer is striated, and seems to consist of parallel fibres extending from the convex to the concave side, and indicating a tendency to crystallization. The phosphate is combined with an animal matter, which is probably the same as that which deposits with the phosphate of lime in the urine evacuated from the body. It chars by heat giving an odour of burnt horn; it burns white, and at last fuses. This latter circumstance distinguishes the neutral phosphate of lime from the basic or common earthy phosphate, but it must be ascertained that the fusibility is not caused by an admixture of phosphate of magnesia. Its powder dissolves much easier in nitric and chlorohydric acids than that of calculi of earthy phosphates.

8. *The double phosphate of ammonia and magnesia* never forms the sole ingredient of calculi, but is not infrequently found as their chief ingredient. Such calculi are almost always white, with an uneven surface covered with small shining crystals. Their structure is not laminated. They feel rough to the touch, and are easily broken and pulverized. In a few cases these concretions have been found hard, semi-transparent and with a crystalline fracture. They dissolve easily in acids and precipitate again by alkali with the ordinary characters of this salt. Caustic potassa liberates ammonia, extracts phosphoric acid, and leaves the magnesia undissolved. Heated on platinum foil

they exhale ammonia, blacken on account of their animal matter, then become gray and at last fuse to an enamel, which has a red colour, if mixed before fusion, with a little nitrate of cobalt.

9. *Basic phosphate of lime* (earthy phosphate of lime,) *with a mixture of double phosphate of ammonia and magnesia* forms, next to lithic acid, the most ordinary material of calculi. Their formation occurs when the urine is alkaline, or at least neutral. They are white, chalky, and earthy, often very large, and sometimes exhibit in their small cavities shining crystals of double phosphate of ammonia and magnesia. They rarely have a laminated structure. They are easily recognised by their great fusibility before the blow-pipe, which induced Wollaston to call them fusible calculi. They blacken by heat, and exhale ammonia before fusion. Dilute acetic acid extracts the magnesian salt, leaving the greater part of the salt of lime. They are easily soluble in chlorohydric acid; when this solution is exactly neutralized oxalate of ammonia precipitates the lime, and subsequent addition of ammonia precipitates the double phosphate of ammonia and magnesia. The relative proportion of the two salts varies in these concretions. As the salt of lime predominates their fusibility diminishes to perfect infusibility. If the salt of magnesia predominate they fuse with difficulty but are never infusible. They sometimes contain lithate of lime, which may be extracted by caustic potassa, filtering the solution

and supersaturating it with chlorohydric acid which precipitates the lithic acid.

The above mentioned ingredients of urinary calculi are also the common ingredients of urine; others will now be considered which do not occur in it when the body is in a healthy condition.

10. *Carbonate of lime* is a rare ingredient of human calculi, but, as we will see presently, the more common ingredient of the calculi of herbivorous animals. Human concretions composed of this salt are white or gray, and sometimes yellow, brown, or red. The carbonate of lime is always combined with an animal matter, to which their colour is due, and which chars by heat with the odour of burnt bone. The formation of these concretions requires the urine to be alkaline, and the ordinary phosphates to be absent. They are easily recognised by their solubility in chlorohydric acid with effervescence, and by leaving caustic lime when ignited by a sufficiently strong heat.

Proust found a calculus consisting only of carbonate of lime with a trace of lithate of lime. Another, weighing seven ounces consisted, according to him, of 0·8 carbonate of lime, and 0·2 basic phosphate of lime without a trace of lithic acid. Afterwards, concretions of this kind were found by Cooper, Prout, Smith, and Fromherz. The latter found by analysis 0·91 carbonate of lime; 0·03 phosphate; 0·04 albumen and brown colouring matter with a trace of oxide of iron. The nucleus of the calculus consisted of a piece of quartz.

11. *Carbonate of magnesia* very probably always occurs in calculi of carbonate of lime, as it is easily overlooked when not particularly sought for. Lindbergsen examined a calculus consisting of: lithate of soda, 9·77; basic phosphate of lime, 34·74; double phosphate of ammonia and magnesia, 38·35; carbonate of lime, 3·14; carbonate of magnesia, 2·55; albumen, 6·87; water and loss, 4·58.

12. *Oxalate of lime* is a frequent ingredient of calculi, especially of those obtained from children. They generally present an unequal surface like a mulberry, and have hence been called mulberry-calculi. They have a dark, blackish-green, or brown colour, which Marcet ascribed to blood effused on them from time to time in consequence of the irritation which their sharp, angular tubercles produce in the urinary passages. I have also had occasion to observe that the urine became bloody when calculi of this kind were descending from the kidneys. Sometimes they have a light colour and are very small, resembling hemp-seed. I have also seen them white and light-yellow, forming a firm aggregation of sharp-edged crystals. The dark colour does not seem to be owing to blood, but rather to the same animal matter which deposits from the urine with other insoluble salts of lime. The quantity of this substance is by no means small; I do not know that it has ever been determined, though it might easily be done by calculating the quantity of lime remaining after

ignition. If a dark coloured calculus of oxalate of lime be heated before the blow-pipe on platinum foil, it swells up, chars, smells of burnt horn, and after perfect ignition of the carbonaceous mass leaves caustic lime, which slakes by the addition of a drop of water, exhibiting a strong alkaline reaction without dissolving. These calculi when powdered are dissolved by digestion with chlorohydric acid, and the salt again deposited in small crystals by evaporation. Caustic potassa extracts part of the animal matter without acting on the salt, but carbonate of potassa decomposes it, leaving a residue of carbonate of lime. The animal matter follows the acid, combining with the oxalate of potassa.

It is not known how oxalic acid enters the urine although it would be of importance to know and avoid the circumstances which favour its formation. It is known, however, that the frequent or daily use of acid vegetables, such as *oxalis acetosella* or *rumex acetosa*, which contain free oxalic acid or its acid salt, causes the formation of gravel of oxalate of lime, which ceases as soon as the use of the vegetables is discontinued. But there are other unknown circumstances which seem to assist their formation without causing any apparent disturbance of the health.

13. *Organic matters*.—Besides the occurrence of fibrin, albumen, casein, and mucus as ingredients of most calculi, (without the possibility of determining by chemical analysis which of them

originally existed in a calculus,) Marcet has found one which seemed to consist nearly altogether of one of these substances. It had the appearance and consistence of yellow wax. Its surface was uneven without roughness, and its structure was formed of radiating fibres somewhat elastic. It burned with the smell of horn and left a porous coal. It was insoluble in water, alcohol, and chlorohydric acid, but soluble in caustic potassa, from which it could be precipitated by chlorohydric acid. Nitric acid dissolved it, but with more difficulty than lithic acid or cystin. With acetic acid it swelled at first, and afterwards dissolved by ebullition; the solution gave a precipitate with ferro-prussiate of potassa like fibrin. Marcet concluded from this, that this calculus consisted of fibrin, but its solubility in nitric acid belongs neither to fibrin nor albumen.

Morin found by analysis of a calculus extracted from a man sixty-one years of age, an organic matter in combination with phosphate of lime. In the nucleus of the calculus it amounted only to ten per cent.; in the second layer to eighteen; and in the third, it amounted to seventy per cent. of the weight of the calculus. Alcohol extracted some fatty matter. It was slightly soluble in acetic acid, but more so in nitric acid. In caustic potassa it swelled up, became slimy, and part of it dissolved. In this case as in that of Marcet, the animal matters had all the properties of hardened mucus. From what I have said in another part

of this work, it may be seen that it has the chemical properties of protein substances with the characteristic difference of dissolving in nitric acid. Scharling has examined a calculus from the museum at Copenhagen, which weighed 255 grains, and was extracted from the bladder of a man after death. It had a fibrous texture which it retained by moistening with water when rubbed in a mortar, although it was brittle and easily pulverized when dry. Ether and alcohol extracted fat; potassa dissolved a protein substance insoluble in nitric acid. It seemed to be composed of 55.36 per cent. of fibrin or albumen, and 44.64 per cent. of earthy phosphate of lime.

Several chemists have also found that by treating the powder of dry calculi with ether or alcohol, small quantities of fat were extracted from human concretion, and both fat and resinous matter from calculi of other animals; these substances were probably altered vegetable matters derived from the food and on their way to be evacuated with the urine.

14. *Silica*.—This substance must be mentioned as the rarest ingredient of calculi, since Fourcroy and Vauquelin found it in only two specimens out of six hundred. In one of them they found only a small quantity of silica; the other had a nucleus resembling a mulberry calculus, and consisted of 0.66 silica, and 0.34 animal matter. By burning away the latter, the silica remained, recognisable by its chemical properties. A third instance is

recorded by Venables, who found silica in the gravel of a woman.

Calculi have been divided into different classes and orders according to their formation from one ingredient, or from several intimately mixed, or from several alternating layers of different composition. But since such mixtures or alternating layers do not depend on permanent causes, but are varied in numerous ways according to incidental circumstances, such as the general state of health of the individual, his manner of living, diet, and use of medicine, I pass over such divisions and merely remark that mixtures of several substances and alternations of differently composed layers in one and the same calculus very often occur.

English physicians who have had the opportunity of seeing many large collections of urinary concretions, have endeavoured to ascertain their relative frequency of occurrence. It appears that calculi composed of lithic acid are the most common in England. Then the fusible calculi, especially if those cases are added in which one of the earthy salts occurs alone or in prevailing quantity; then such as consist of alternating layers of lithic acid, phosphate and oxalate of lime. They found, for example, amongst a thousand calculi,

372 composed of lithic acid alone, or with a small admixture of lithate of ammonia, and oxalate, or phosphate of lime;

253 composed of earthy phosphates (fusible calculi;)

233 composed of alternating layers of lithic acid, oxalate of lime, and earthy phosphates ;

142 composed of oxalate of lime.

The more rarely occurring calculi of carbonate of lime, cystin, and silica, cannot enter into such a calculation. The relative proportions, however, vary in different countries according to differences in climate, food, occupations, and customs. Rapp, for instance, found in Wirtemberg, amongst eighty-one calculi, twenty-two composed of oxalate of lime alone, and thirty-four in which this salt was mixed with other substances, (i. e. fifty-six containing oxalate of lime ;) only seven of lithic acid alone, and nine of lithic acid mixed with earthy phosphates ; seven fusible calculi, one of lithate of ammonia, and one of earthy phosphates with 13 per cent. of carbonate of lime.

Not only man, but the lower classes of animals also suffer from calculi. The ingredients which are not ordinarily found in their urine, or only in small quantities, are often the cause of their calculi, as, for instance, lithic acid in the carnivorous and earthy phosphates in the herbivorous animals ; though carbonate of lime is the most common material in the concretions of the latter.

Lithic acid, phosphate of lime, double phosphate of ammonia and magnesia, oxalate of lime, cystin, and mucus constitute the chief ingredients of the calculi of dogs. Lassaigne analyzed a calculus composed according to him of cystin ; the

specific gravity was 1.577, and it contained 97.5 per cent. of cystin, and 2.5 per cent. of phosphate and oxalate of lime. I refer to what has already been said under *cystin* to the doubt expressed whether this substance was in reality cystin.

Calculi from horses consist of carbonate of lime and magnesia, phosphate of lime, double phosphate of ammonia and magnesia, and fat; Bucholz found in such a calculus from a horse, 0.94 of a resinous, brownish green matter, soluble in six times its weight of alcohol, but insoluble in ether, water, and chlorohydric acid. Treated with a concentrated lye of potash, it combined with it, and was increased by 0.4 of its weight. The resinate of potassa thus formed was insoluble in the lye of potash, but perfectly soluble in pure water. It was easily dissolved by dilute caustic ammonia, and precipitated by chlorohydric acid. The solution in alcohol became turbid by water, of a dark green colour by chloride of iron, and precipitated in large flocculi by a solution of glue.

Calculi from oxen, sheep, swine, and rabbits, consist of carbonates and phosphate of lime and magnesia, and of double phosphate of ammonia and magnesia. Wurzer analyzed a calculus from the urinary organs of an ox that had died in consequence of it. It contained carbonate of lime, 36.8; phosphate of lime, 6.2; oxide of iron, 1.8; silica, 38.2; animal matter, 13.8; water and loss, 3.2; whence it may be seen that calculi of silica occur also in animals.

According to Angelini a calculus from a pig gave a garnet red colour to alcohol. After evaporation, and washing the residue with water, ether extracted a red matter, leaving a greasy mass which was not saponified by caustic potassa, or at least with difficulty, but which melted in boiling water. The red matter extracted by ether resembled a resin, and was soluble in alcohol, fixed and volatile oils. It dissolved in caustic potassa with a yellow colour, and in its carbonate with a green colour. Great excess of alkali prevented the solution of the combination. From the alkaline solution it was precipitated by sulphuric and nitric acids, which restored the red colour, and redissolved the precipitate when added in excess. The precipitate combined with chlorohydric acid forming a scaly mass, from which the acid could be washed by water, which also restored the red colour. By heat it generated red fumes and exploded(?)

According to Morand, rats are so frequently affected with calculi that it is rare to meet with one whose kidneys do not contain them. Their calculi consist of oxalate, phosphate, and carbonate of lime.

Fish also are not exempt from calculi. They occur not unfrequently in the Huso, (*Acipenser Huso*) and the Sturio (*A. Sturio*), especially in the oldest and largest, in whose urinary organs calculi of considerable size and from $\frac{1}{4}$ to $\frac{1}{2}$ lb. weight, have been found. They are most fre-

quently found in the Huso taken at fisheries on the Caspian sea, and more particularly near Astrachan. They are generally flattened, with unequal depressions; exteriorly they are of a dirty yellowish colour, and they have considerable hardness and weight. According to Klaproth their specific gravity varies from 2.243 to 2.265. They are very firm and brittle, and their fracture exhibits a concentric, radiating, crystalline structure, strongly resembling the broken surface of a stalactite of lime. Transverse scales are also observed. In their interior they are almost colourless. Klaproth examined one of more than seven ounces in weight. Before the blow-pipe it first burned gray and then white, with the smell of burning animal matter, and then fused into a white enamel. It dissolved without effervescence in nitric acid. The analysis gave: phosphate of lime, 71.5; sulphate of lime, 0.5; albumen, 2.0; and water, 24.0.

As the formation of calculi in the urinary organs is, in general, a consequence of an abnormal chemical composition of the urine, and as this may be altered by the use of substances which become accidental ingredients of the urine, the cure formerly attempted consisted in an endeavour to remove the cause of their formation. This succeeds when the calculi consist of lithic acid, since the use of alkaline carbonates or of the neutral salts of potassa and soda with vegetable acids, renders the urine alkaline and retains the lithic acid in solution. By this treatment calculi and gravel formed

in the kidneys are detached and removed even when they are composed of oxalate of lime and earthy phosphates. But when the urine is alkaline and deposits these last mentioned substances nothing can be effected by the use of mineral acids since they do not make the urine acid. Oxalic, citric, and tartaric acids are certainly capable of producing this effect, but on the other hand they easily produce concretions from their salts with lime.

The case, however, is altered when a calculus has been already formed. The urine of such patients, even in its healthy state, deposits a portion of its sediment on the calculus in the bladder, and the remedies employed often produce no other effect than an alternation of differently composed layers and an increase in the size of the calculus, although perhaps its growth may occasionally be retarded. If renal concretions may sometimes be cured by remedies selected on chemical principles, vesical calculi can only be remedied by removal, and the sooner this is done the better it is for the patient. It has been proposed to dissolve it, but this would make it necessary to ascertain the composition of the calculus while it is still in the bladder. This can only be done approximately, by presuming it to consist of lithic acid or oxalate of lime when the urine is acid, and of earthy phosphates when it is alkaline or neutral. The best injection is a tepid solution of one part of carbonate of potassa with from 90 to 100 parts of water

mixed with a little mucilage, as it acts on all kinds of calculi. Caustic potassa acts too severely on the bladder and urethra. A solution of borax may also be used for calculi of lithic acid. The solution should be retained in the bladder as long as possible, and examined after evacuation, to ascertain whether any thing has been dissolved, but the ingredients of the urine which has been secreted in the mean time, should be taken into the account. It is very probable that chlorohydric acid diluted with a large quantity of mucilage would dissolve calculi of earthy phosphate of lime and cystine. Experiments made for dissolving calculi have not proved so successful as was expected; but I am fully convinced that they have not been repeated sufficiently often to ascertain and avoid such accidental circumstances as cannot be foreseen and which might impede their success. Dumas and Prevost have made successful experiments on dogs of decomposing calculi of earthy phosphates by introducing the insulated conductors of a voltaic column into the bladder, placing them in contact with the calculus, and passing an electric current through it. When the conductors were combined with the poles of a powerful voltaic series, the ingredients of the calculi were separated, but combined again in the urine and were evacuated as precipitate.

The surest way however of getting rid of calculi is by resorting to mechanical means, such as

lithotomy, or lithotrity. These are not to be considered here.

Examination of the Urine.

The examination of the urine is highly important to physicians. It is made partly by the immediate application of tests to the urine and partly by evaporation. The former is of more importance to physicians, since they frequently lack either time or the special chemical knowledge necessary for the examination by evaporation. It is to be regretted that we know so few tests applicable to this purpose, and therefore the discovery of others will be very valuable.

Nitric acid is used to discover the presence of (a.) *Lithic acid*. A few drachms of the test should be added to half a pound of the urine, which should then be allowed to stand in a glass vessel for twelve hours; on the removal of the liquid, if lithic acid be present, the inside of the vessel will be found covered with a grayish white coating, or with small reddish brown crystals. (b.) *Albumen* is known to be present when nitric acid causes a white or grayish white flocculent precipitate, which when washed is soluble in caustic potassa and not precipitated from this solution by acetic acid. (c.) *The colouring matter of the bile* is present when the urine, mixed with an equal volume of nitric acid, becomes at first greenish, then dark green, then pink, and afterwards brown. But

these changes cannot be perceived when there is only a very small quantity of the colouring matter present. In partial obstructions of the liver, when the bile enters the blood through the absorbents of the obstructed part, the bilious matter may be detected in the urine even before the disease is indicated by discolouration of the skin or sclerotic. But for this purpose it is necessary to evaporate the urine and treat it with anhydrous alcohol; the extract obtained by evaporating the alcohol is to be mixed with nitric acid, when it will show distinctly the reaction of bilious matter, since the greater part of the colouring matter of the urine has been removed. (*d.*) *Urea* is sometimes in excess, sometimes deficient, sometimes entirely wanting in the urine. It is important to physicians to be able to distinguish these cases. According to Prout, the urine sometimes may contain so much urea as to afford crystals of the nitrate, without previous evaporation, after the lapse of a few hours from the time of adding nitric acid to it in excess; he states that this is the case when the specific gravity is as high as 1.025 and 1.030, without the existence of diabetes. According to my own experiments, urine of 1.03 sp. gr. evaporated at 175° F. to three-fourths of its original volume, and mixed with equal portions of nitric acid of 1.25 sp. gr. deposited at 60° F. no nitrate of urea; evaporated to half its volume it yielded a few crystals only at the end of five or six hours; evaporated to one-third of its volume

the liquid became filled with crystalline scales, and when only one-fourth of the original volume remained, it became a solid mass of crystals at the end of a few hours. The best method of performing this test is the following. A glass cylinder with a height double the diameter, such as a tumbler, should be graduated on the outside in fractions of its own volume. The urine is to be evaporated in this in a water-bath; at certain points of the evaporation a few drops are to be removed and mixed with an equal number of drops of nitric acid of 1.25 sp. gr. in a test tube four inches high, and should then stand for six hours. This test cannot be performed on a watch glass, because the evaporation during the experiment will be very considerable, and will cause the deposition of crystals. It is also to be observed that comparative tests are to be made at the same temperature, as a liquid will often give crystals at 32° F. which would not deposit any at 60° F.

Ammonia precipitates the earthy phosphates dissolved in the free acids of the urine; it may sometimes be important to ascertain their relative quantity. Ammonia is also used for determining the relative acidity of the urine. For this purpose a dilute solution is employed of known strength, ascertained by saturating it with chlorohydric acid and weighing the sal-ammoniac obtained by evaporation. A certain volume of urine is to be mixed with an infusion of litmus, in which the excess of alkali has been saturated with acetic

acid until it has become distinctly red; the ammonia is then added by drops from a graduated measuring tube until the blue colour is restored. The liquid must be allowed to settle between the last additions, on account of the precipitate which is produced. The quantity of ammonia employed affords a measure of the acidity of the urine.

Lime water will detect the presence of soluble phosphates by precipitating phosphate of lime. Human urine should be previously saturated with ammonia free from carbonic acid, and filtered, in order to remove the earthy phosphates dissolved in the free acids. Urine of the lower animals should first be saturated with chlorohydric acid, and gently heated before the addition of lime water, in order to remove the carbonic acid.

Oxalate of ammonia precipitates the lime of the urine, especially on the application of moderate heat. The subsequent addition of ammonia precipitates the double phosphate of ammonia and magnesia. If ammonia produce no precipitate, a solution of phosphate of soda should be added to ascertain whether the want of precipitate is owing to the absence of magnesia or of phosphoric acid.

Chloride of barium, or better, *Acetate of baryta* will discover the presence of sulphates. When the urine is neutral or alkaline it should be acidulated with acetic acid before the test is added.

Neutral acetate of lead, after the separation of the previous precipitate by filtration, detects the

presence of phosphoric acid, which precipitates as basic phosphate of lead. For the effectual removal of chloride of lead the precipitate must be washed with boiling water and fused before the blow-pipe.

Solution of alum will produce a cloudiness in urine when it contains albumen or fibrin.

Solution of perchloride of mercury produces no change in urine containing a free acid if no albumen or casein be present; but it will detect even small quantities of these substances. From a neutral urine it precipitates several of the common ingredients of urine.

Nitrate of silver precipitates chloride of silver and phosphate of silver. The latter is dissolved by nitric acid.

Tannic acid, especially as an infusion of galls, precipitates at least two of the ingredients of urine: mucus in solution and the extractive matter which is precipitated by neutral acetate of lead. In healthy urine the precipitate is very inconsiderable, at most from 0.002 to 0.003 of the weight of the urine; and it is seen distinctly only after some time has elapsed from adding the test. A copious precipitate indicates the presence of albumen.

Litmus paper.—The blue litmus paper is used to detect acidity, the red, alkalinity. It must be remembered that a blue litmus paper dipped in urine, without immediate reaction, becomes red on drying from the ammoniacal salts of the urine.

Ferment is used to discover the presence of

sugar by the fermentation it induces when the latter substance exists in the urine. The quantity of carbonic acid generated and collected over mercury, or if this cannot be done, the gas passed through basic acetate of lead and precipitated as carbonate of lead will afford, when compared with the quantity of urine employed, a relative scale of the quantity of sugar in the urine.

Some general rules for the quantitative analysis of the urine.—The quantitative analysis of this liquid is very difficult. It is impossible to determine all the ingredients from one portion, and the urine of the same individual never remains the same, at least it is certainly variable in its amount of water. It must therefore suffice, when the question regards the amount, to find the quantity of substances in portions of the urine given at different times; for this reason an accurate result can never be obtained. This analytical examination, however, is seldom required except for the determination of certain ingredients without reference to the rest.

a. The specific gravity of the urine is first ascertained, which gives an idea of its concentration. The spontaneous sediment is then separated by filtration on a weighed filter, and washed, dried, and weighed. It is either mucus, in which case its weight is inconsiderable, or it consists of a red, ochrey or gray powder. It is to be boiled with alcohol, which dissolves the red colouring matter and lithate of ammonia, which may afterwards be

separated, although incompletely by water. If the sediment be yellow it is extracted by acetic acid, which dissolves the yellow colouring matter. Caustic potassa then dissolves lithate of potassa, leaving phosphate of lime, or silica, or a mixture of both. The lithic acid is obtained by precipitating the alkaline solution with acetic acid, and the subsequent addition of ferro-prussiate of potassa to the acid solution after it has been filtered, precipitates the mucus only slightly increased in weight by the cyanogen and iron.

b. To the filtered urine caustic ammonia is to be added in slight excess. The precipitate should be filtered, washed, and weighed. The animal matters are to be burned away, the residuum again weighed, and the phosphates of lime and magnesia separated from one another by the ordinary methods.

c. The filtered urine and the wash water are evaporated in a water-bath as far as possible, and the residue weighed, which can best be done in the evaporating capsule. It is then treated with alcohol of 0.833 as long as any of it is dissolved; the remainder should be dried in a water-bath and weighed, by which the weight of the soluble matter is obtained. The alcohol should be distilled, the remainder dried in a water-bath as long as it gives out moisture and then treated with anhydrous alcohol. It is important to remove all the water, otherwise the alcohol solution will contain salts of potassa and soda; it is also necessary that

the remainder be perfectly washed with warm anhydrous alcohol before it is dried and weighed. The anhydrous alcohol should not be removed from the insoluble matters until it has been cooled down to 32° F.

d. The anhydrous alcohol now contains urea, sugar, the peculiar extractive matter, lactic acid, lactate and chloride of ammonium, together with fat and the acid matter soluble in ether. The alcohol is now to be perfectly distilled away in a water-bath and the residue treated with warm ether as long as fresh portions of it dissolve any thing. The ethereal solution is to be distilled and the residue weighed. It may contain saponified fat and small quantities of lactate of lime and ammonia. I refer here to what I have already said on the organic constituents of the urine.

The mass treated with ether is to be dissolved in a small portion of water, warmed to 104° F., and mixed with oxalic acid, free from potassa, as long as a new addition of the acid is dissolved. On cooling the solution deposits brown crystals of oxalate of urea, which are to be drained in a funnel and washed with a little water. This water should be evaporated with the mother-water for a new crystallization. Should the mother-water have lost the strong acid taste, it must be warmed and more oxalic acid dissolved in it. As soon as it becomes viscid by evaporation and is still sour, it is to be drained from the crystals, which should then be laid on folds of bibulous paper, and pressed.

The crystals are to be dissolved in water, mixed with carbonate of lime and the solution of *urea* thus obtained, evaporated in a water-bath to dryness, and *weighed*. It should now be dissolved in boiling anhydrous alcohol, and if any matter remain undissolved, its weight must be deducted from the weight of the urea. It may be oxalate of ammonia, and, from some inaccuracy in the analysis, oxalate of potassa, both of which retain some urea.

The paper in which the crystals were pressed is now to be washed with water, which, after having been somewhat concentrated by evaporation, is to be added to the mother-water. This is then saturated with carbonate of lime, the neutral solution filtered, mixed with the wash-waters from the oxalate of lime, evaporated in a water-bath to dryness and the residue weighed. This contains the extract of urine soluble in anhydrous alcohol, chloride of ammonium, lactate of ammonia with a little lactate of lime. The latter remains in combination with a portion of extract insoluble in anhydrous alcohol; it is to be dried and weighed. Afterwards it should be dissolved in water, precipitated by oxalate of ammonia, and the precipitate, made caustic by ignition, corresponds to an equivalent of ammonia which was in combination with the oxalic acid. The solution in anhydrous alcohol should be evaporated, mixed with water, and precipitated by nitrate of silver. This precipitate is now to be washed with water which

has been acidulated with nitric acid; and the silver reduced from it by iron or zinc with addition of a little chlorohydric acid; from the weight of the reduced silver, the weight of the chloride of ammonium is reckoned. Nothing can be computed from the weight of the dry chloride of silver, since it contains much extractive matter. Besides the separately obtained weights of the chloride of ammonium, urea, and lactate of ammonia, there is still wanting that of a mixture of extract soluble in alcohol, and lactate of ammonia with a small quantity of lime, which cannot be any farther separated, but wherein the extract forms the principal mass.

If the urine contains sugar, it is separated in the manner already mentioned, by mixing the extract obtained by alcohol of 0.833 with basic acetate of lead as long as it yields any precipitate. This is to be filtered and washed; the liquid, freed from lead by sulphuretted hydrogen, is to be evaporated to a syrupy consistence, and put in a cool place for crystallization; after which it is to be dried *in vacuo* over sulphuric acid and the residuum treated with anhydrous alcohol, which does not dissolve the sugar, or at least only a small quantity of it. Formerly it was proposed to estimate the quantity of sugar, from the carbonic acid generated by fermentation from a certain quantity of urine; but Liebig has shown that when the urine also contains urea it will be decomposed, and when the last portion of carbonic acid is ex-

pelled from the liquid, it is followed by carbonate of ammonia; on which account the result is much less accurate than the approximate result obtained by the direct separation of the sugar.

e. The portion of extract, obtained by alcohol of 0.833, which is insoluble in anhydrous alcohol, (*c.*) is to be incinerated. The residuum contains chloride of potassium, chloride of sodium, and carbonate of soda; the latter is derived from the lactate of soda. They are separated by ordinary methods, and their weight, after the deduction of that of carbonic acid, shows how much lactic acid and extractive matter have been destroyed by the incineration.

f. We come now to the portion of urine which was altogether insoluble in alcohol of 0.833. (*c.*) After its weight has been ascertained it is to be dissolved in water, filtered from the insoluble matters, acidulated with acetic acid and precipitated by acetate of baryta. The precipitate is to be dried in a water-bath, completely calcined and weighed. The loss by incineration shows the quantity of animal matter combined with it. The residue from the incineration is sulphate of baryta, from which the quantity of sulphuric acid may be computed. After the solution has been precipitated by acetate of baryta, it should be mixed with ammonia until it has an alkaline reaction, and then precipitated by acetate of baryta. The precipitate is sub-sesquiphosphate of baryta. It is to be washed, dried in a water-bath, and weighed.

By calcination and weighing, the weight of animal matter is obtained; and the calcined phosphates are then converted into sulphates, from which the quantity of phosphoric acid is computed. The solution precipitated by acetate of baryta is to be neutralized as accurately as possible by acetic acid, and precipitated by neutral acetate of lead. The precipitate is to be treated with sulphuretted hydrogen, and this solution evaporated to dryness and weighed. It gives the weight of the animal matter in the urine, which is principally precipitated by an infusion of galls.

g. The remaining solution is precipitated by basic acetate of lead. The washed precipitate is to be treated with sulphuretted hydrogen, the excess of the latter expelled, the free acid of the solution saturated with carbonate of ammonia, evaporated to dryness, and the ammoniacal salt extracted by alcohol of 0.833. The remainder should be weighed. The alcoholic solution is to be evaporated, redissolved in water, and precipitated by nitrate of silver. The precipitate is to be fused, when it will correspond to an equivalent of chloride of sodium, which the alcohol could not extract from the remainder of the urine.

h. The solution precipitated by basic acetate of lead is to be treated with sulphuretted hydrogen, the solution evaporated to perfect dryness and the acetates extracted by anhydrous alcohol. That

which remains undissolved is to be dried and weighed, (see page 93.)

i. The solution in alcohol is to be evaporated, the salts calcined, the remaining bases dissolved in water, saturated with chlorohydric acid, weighed and separated into potassa and soda by chloride of platinum. The extent of the insufficiency of these to saturate the ascertained quantities of phosphoric and sulphuric acid shows how much phosphoric acid was combined with ammonia, for the most part in the form of biphosphate.

k. The insoluble from *f*, is lithic acid, mixed with a small quantity of lithate of ammonia, mucus of the bladder, and silica. It is to be treated with dilute caustic potassa, which dissolves the two former, and which may be separated by the method already spoken of in the analysis of the sediments. The remaining silica is gray, it exhales an ammoniacal odour in burning, and should therefore be weighed both before and after the calculation. It must be tested by chlorohydric acid for the presence of phosphate of lime.

This should be the way of proceeding with the analysis of the urine. Perhaps the time may come when it will seem to be very imperfect.

Examination of urinary concretions.—The calculus is to be sawn in two, in order to separate the strata differing in appearance. Tests by the blow-pipe, on charcoal or platinum foil, show, in accordance with the already mentioned reactions

of the ingredients of calculi, what is to be expected. In order to save the reader who wishes to use the blow-pipe for such examinations, the trouble of collecting the reactions from the previous details, I will state all that is known of the behaviour of calculi before the blow-pipe.

1. *Calculi of lithic acid*.—Heated by themselves on charcoal or platinum foil they char and fume, exhaling animal odour; in the outer flame they continually diminish in size. After awhile they burn with increased lustre and when removed from the flame, continue ignited, leaving, finally, a very slight trace of a strongly alkaline white ash.

Very often the calculi consist of a mixture of lithic acid with earthy phosphates; when this is the case they are charred and burned, but leave a considerable residue, which is not alkaline, nor soluble in water. Treated with nitric acid and afterwards with ammonia they give the bright red colour which indicates the presence of lithic acid. The remaining ash is either phosphate of lime or phosphate of magnesia, or a mixture of both.

2. *Calculi of lithate of soda*.—This rare ingredient of calculi is oftener found in the concretions of the joints of gouty persons. When heated alone on charcoal they blacken and exhale an empyreumatic animal odour, leaving a gray, strongly alkaline residue convertible into glass by adding a little silex. If the calculus contains earthy salts, as it usually does, the glass becomes white or gray and opaque.

3. *Calculi of lithate of ammonia* before the blow-pipe, behave like those of lithic acid. A drop of caustic potassa will cause them to exhale when gently heated, a strong ammoniacal odour. Care should be taken not to be misled by a slight lye-like ammoniacal odour, which almost all animal matters yield with potassa. These calculi often contain some lithate of soda.

4. *Calculi of phosphate of lime* heated alone on charcoal, blacken, exhale an empyreumatic animal odour, and at last burn white, but do not melt. Otherwise they behave like ordinary phosphate of lime.

The proof that they are not silica is the fact of their swelling up with soda without being converted into glass, and moreover when they are dissolved in boracic acid and melted with iron they give a regulus of phosphuret of iron.

5. *Calculi of phosphate of ammonia and magnesia* when heated alone on platinum foil, smell strongly of hartshorn, blacken, swell, and afterwards burn by increased heat to a grayish white mass. They easily fuse to a grayish white, enamel-like globule.

They dissolve into a transparent glass with borax and salt of phosphorus, but when much of these substances is added, the glass becomes milk-white on cooling.

With soda they fuse into a white swollen slag, which remains infusible on the addition of more soda.

With boracic acid and iron they easily yield a regulus of phosphate of iron.

With nitrate of cobalt they give a dark red glass.

6. *Calculi of a mixture of phosphate of lime and magnesia, or fusible calculi.*—These may be recognised by their giving only a slight ammoniacal odour, which is chiefly derived from destruction of animal matter. They fuse more easily than any other calculi to an enamelled globule, which does not become red, but of a deep brown colour, with nitrate of cobalt.

7. *Calculi of oxalate of lime or mulberry calculi.*—When they are heated alone they sometimes exhale a urinous or animal odour on the first application of heat. The more crystalline become duller and lighter in colour. After gentle ignition they effervesce with a drop of nitric acid, and after a stronger ignition on charcoal they leave behind caustic lime which gives an alkaline reaction with reddened litmus paper, and ordinarily slackens to a powder when moistened with water. The latter does not occur when the calculus contains also phosphate of lime.

8. *Calculi containing silica* on burning leave a gray, infusible, sometimes slaggish ash, which, mixed with a little soda, slowly dissolves with effervescence, to a more or less transparent glass-globule.

9. *Calculi of cystic oxide* behave before the blow-pipe almost in the same way as those of

lithic acid. They readily take fire and burn with a bluish gray flame, exhaling at the same time a peculiar odour somewhat resembling that of cyanogen. They leave an ash, which is not alkaline, and which fuses to a gray-white mass when exposed to a good fire. They differ from lithic acid calculi as well by their peculiar odour when burned as by not giving a red colour with nitric acid.

For special analysis the calculus is to be powdered, dried, and weighed. It is then treated with ether, which extracts the fatty and resinous matters for separate examination. The powder is then boiled with alcohol and examination made of the substances it has extracted. If the calculus is known to consist chiefly of lithic acid, it is to be repeatedly boiled with water. The solution in water may consist of lithates of potassa, ammonia, lime, and magnesia, with a small quantity of phosphates from the urine and animal matters. By evaporation nearly to dryness the lithates separate; they may be decomposed by chlorohydric acid and their bases determined. That which the water would not dissolve should be dissolved in dilute caustic potassa; and what this leaves undissolved should be tested for phosphate of lime, magnesia, oxalate of lime, and silica.

The solution in potassa is precipitated by acetic acid in great excess; the precipitate, when washed and dried, is lithic acid. The solution is evaporated in a water-bath till it loses the smell of acetic acid, and then dissolved in water, which

leaves albumen, mucus, &c., undissolved. The solution in water should be tested for animal matters by infusion of galls, chloride of mercury, chloride of tin, and other tests of this kind.

If it has been ascertained that the calculus contains chiefly phosphate of lime, it is to be treated with ether, alcohol, and boiling water, and afterwards dissolved in chlorohydric acid; the solution is mixed with ammonia till a precipitate begins to appear, and then mixed with a solution of oxalate of ammonia as long as oxalate of lime is precipitated. The solution is then filtered and precipitated by caustic ammonia; the precipitate is double phosphate of ammonia and magnesia. The remaining solution and the precipitate are both to be tested for animal matters.

If the calculus contains oxalate of lime, it is treated, after previous extraction by ether, alcohol, and water, with caustic potassa for the purpose of dissolving the lithic acid and animal matters which are to be farther examined. The powder is then divided in two portions, one of which is calcined, the residuum dissolved in chlorohydric acid, the carbonic acid expelled by ebullition, and ammonia added to discover whether it precipitates any earthy phosphates, which are then to be examined. The other portion of the powdered calculus should be digested with very dilute sulphuric acid, and the solution evaporated. Should it yield a sour syrup it contains either phosphoric, tartaric or citric acid. The two latter have not

yet been discovered, but their presence is not impossible.* It must be ascertained which of them it is.

Calculi of double phosphate of ammonia and magnesia should be treated as calculi of earthy phosphates.

Calculi of cystic oxide are dissolved in caustic ammonia after being treated with ether, alcohol, and water. If any of it remains undissolved in the ammonia it is to be examined. The solution is evaporated and yields to the last drop crystals of cystic oxide.

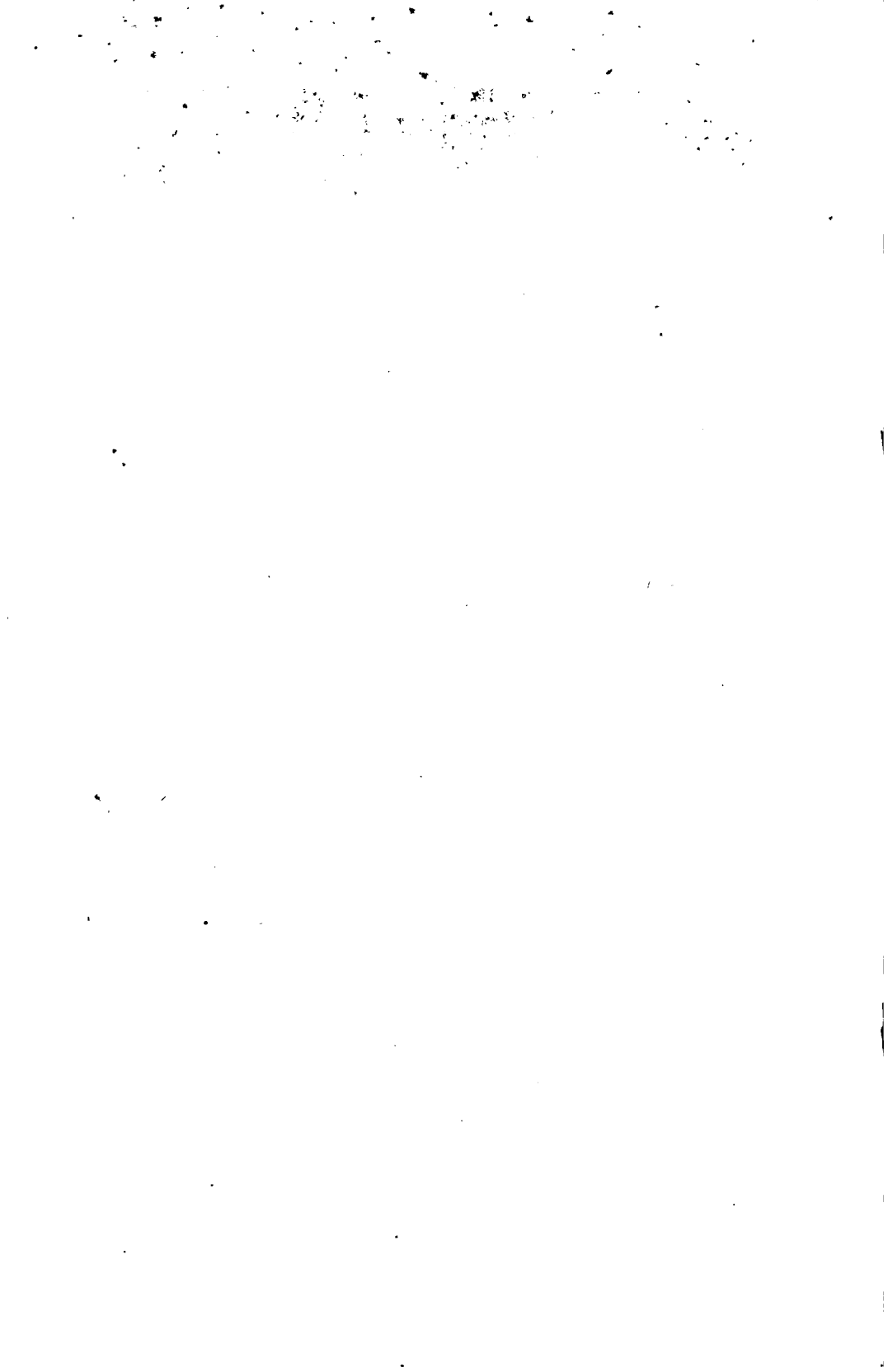
Of course no rules can be prescribed for analysis in cases where the calculi consist of very uncommon substances.

Urine is employed for several technical purposes. It is chiefly used after previous putrefaction, whereby the urea is converted into carbonate of ammonia, for the manufacture of sal-ammoniac, for stamping of cloth, and for preparing or dissolving different colours in dyeing. Urine of cattle is used to moisten saltpetre-earth in nitre manufactories; the nitrogen is gradually converted into nitric acid, which unites with the bases in the

* I once had an opportunity of observing that a diabetic urine which passed spontaneously into an active vinous fermentation, deposited a copious sediment consisting of shining, colourless crystals of *pure tartrate of lime*. The patient, who died shortly afterwards, is not known to have taken any substance containing tartaric acid; it is therefore conjectured that in this case the tartaric acid was formed either in the kidneys or by the fermentation.—WÖHLER.

saltpetre-earth. Finally, the urine is used as one of the best manures for agriculture. Several of the wandering tribes in America are said to evaporate the urine and burn it, for the purpose of obtaining common salt, which they cannot procure in any other way.

FINIS.



TO THE MEDICAL PROFESSION.

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THE ILLUSTRATIONS**

EMBRACING

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IN SMITH AND HORNER'S ATLAS.**

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
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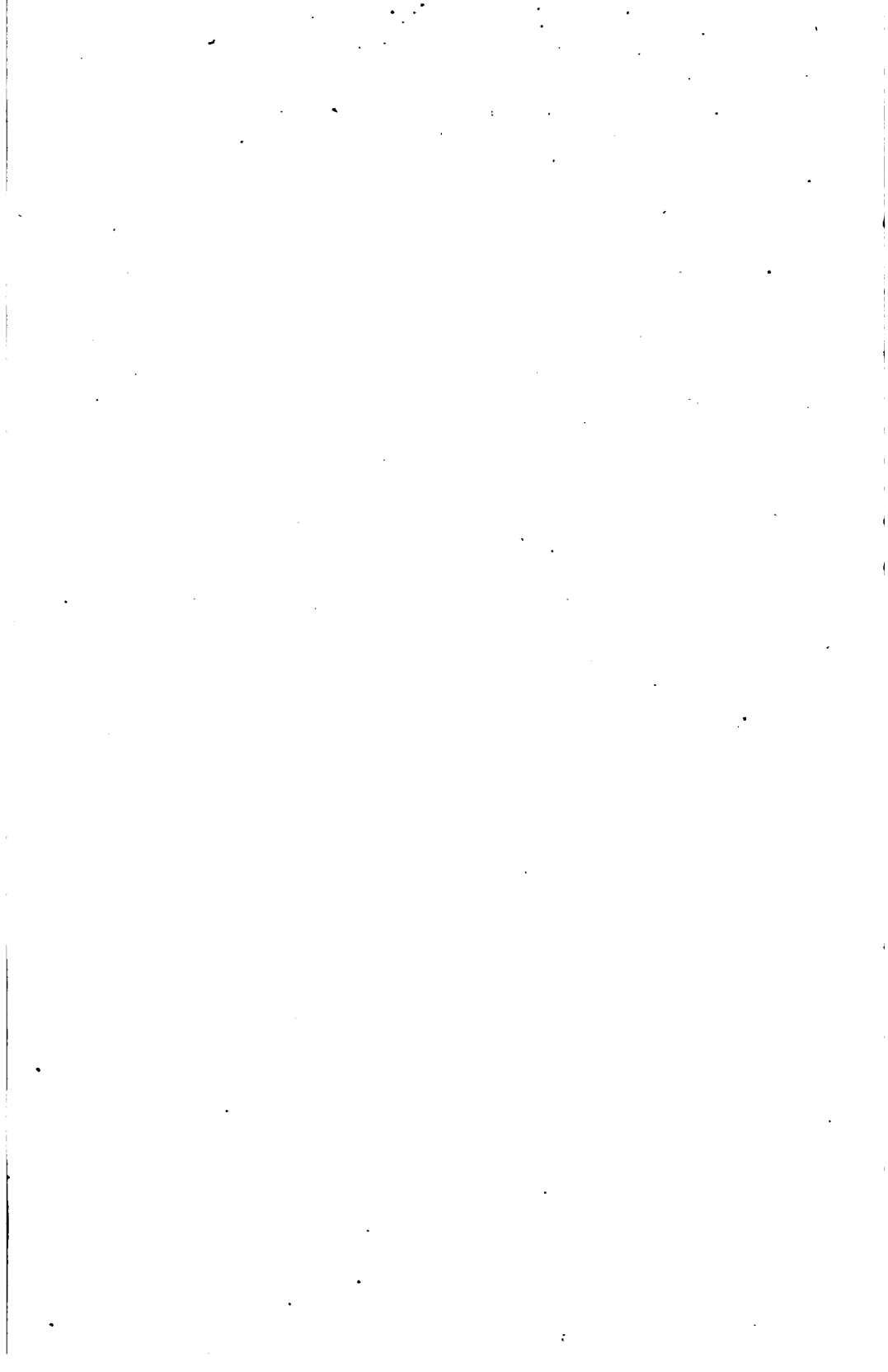
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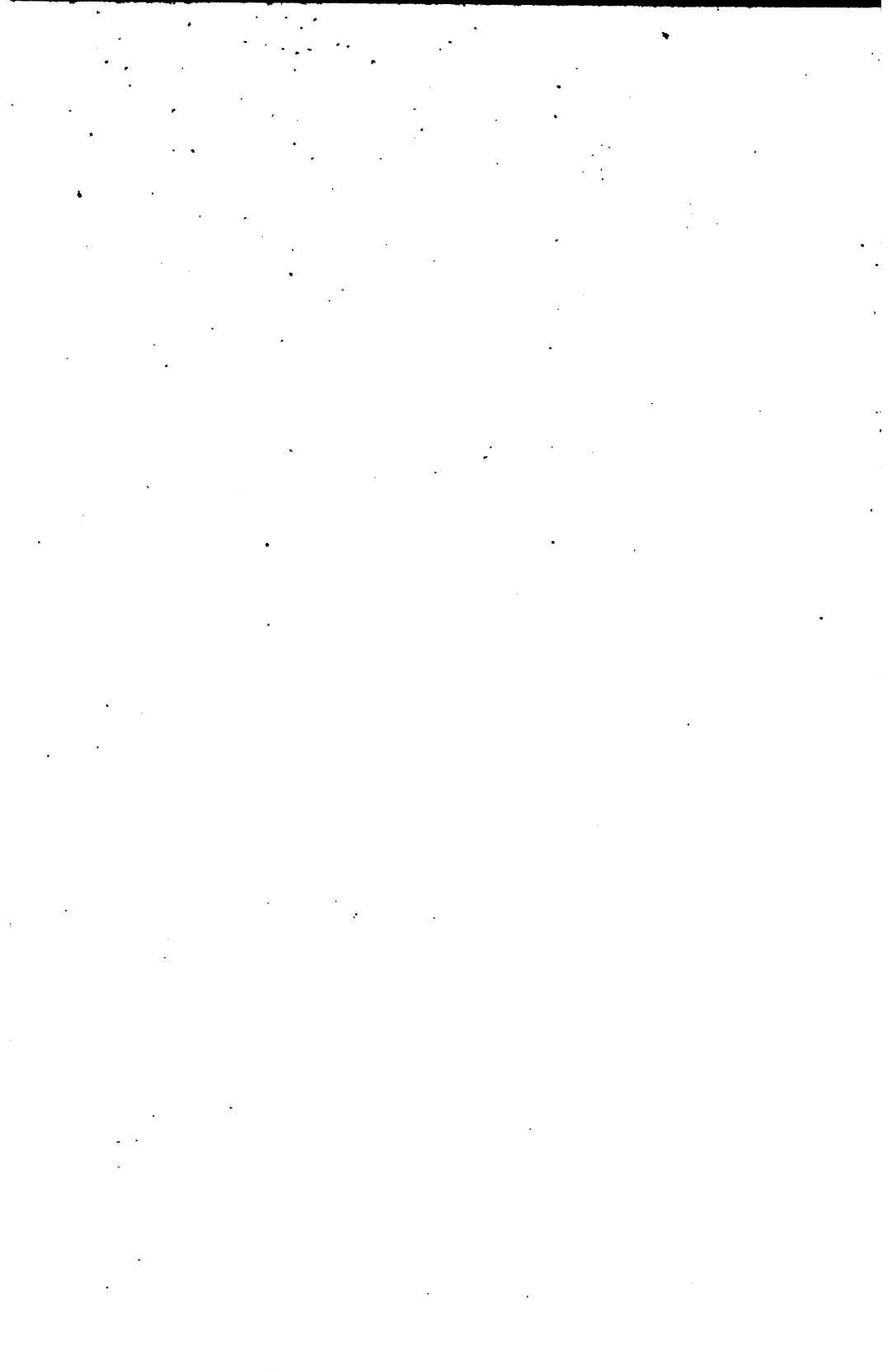
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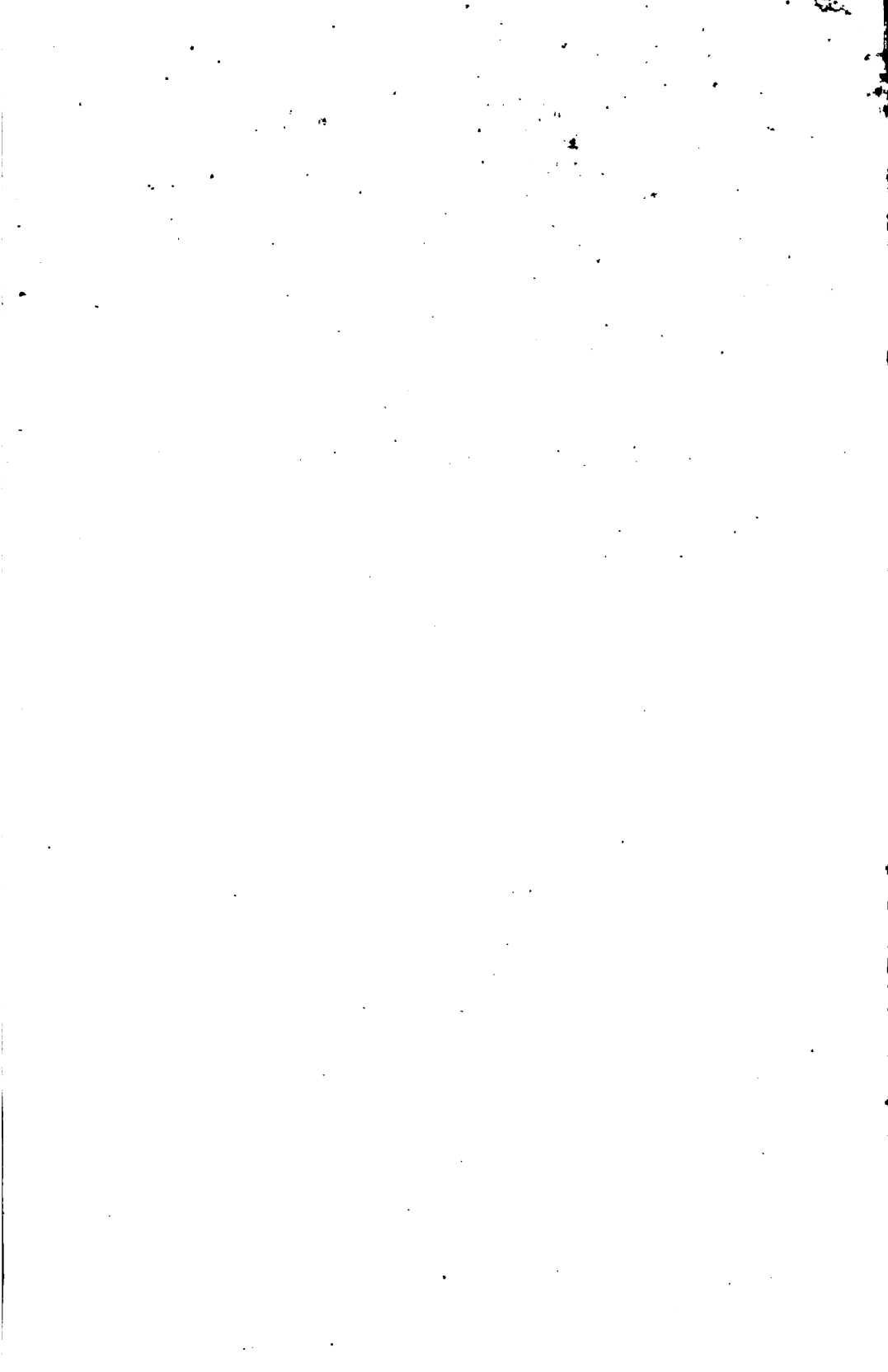
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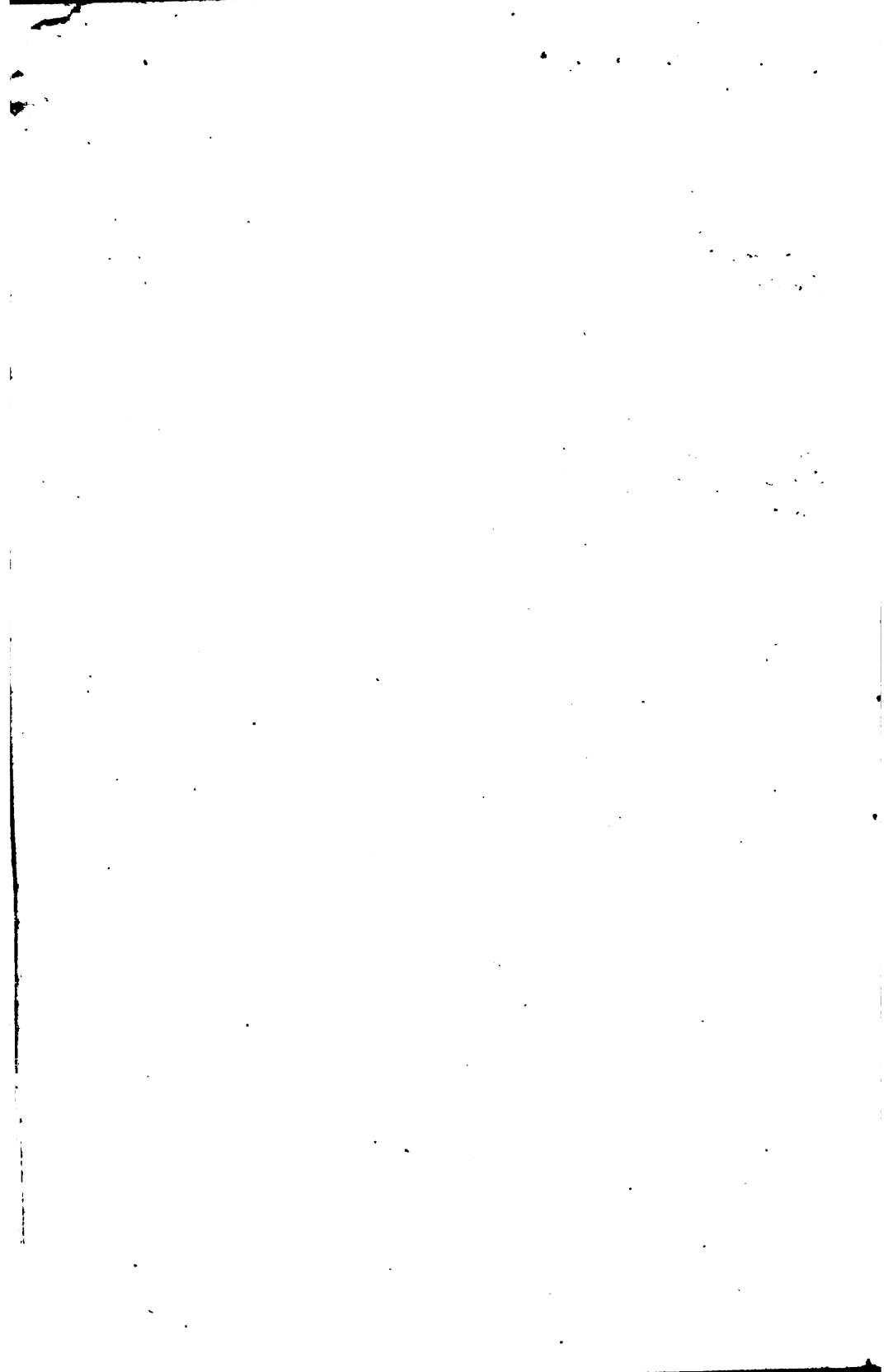
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